Low Pressure Reactions of Sulphur and Sulphur Compounds.

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by

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C O N T E N T S.

INTRODUCTION.

Preliminary Experiments.

During the last four or five years the emission and absorption spectra of sulphur vapour and some of the simple molecules containing sulphur have been successfully analysed (e.g. S_2, SO, SO_2, CS, etc.)[1]. It appeared probable that this knowledge might find useful application in placing the course of some of the simpler gas reactions in which sulphur played a part and it was hoped that theoretical results of some importance in the kinetics of gas reactions might thereby be obtained. A number of preliminary experiments were accordingly carried out and spectroscopic observations made, but, although these results were interesting the special difficulties which were encountered made it undesirable in the circumstances to pursue them beyond the qualitative stage and the description of these experiments is deferred to the end of this thesis.

The reactions which were chosen for detailed study were

(1) The Oxidation of Sulphur at Low Pressures.

(2) The Influence of Foreign Gases on the Lower Critical Oxidation Pressure of Carbon Disulphide.

As both of these reactions are explained on a reaction chain hypothesis, the first section of this /

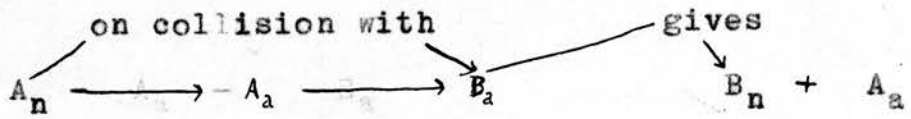
this thesis will give a general survey of the theory of chains and/of the reaction which have been explained by its means.

Chain Theories.

The idea of a chain reaction was first introduced by Nernst[2] to explain the enormously greater yield in the photochemical reaction between hydrogen and chlorine and the amount expected according to Einstein's Law, which states that one quantum of energy gives one primary reaction. In 1923 Christiansen and Kramers[3] showed that the chain hypothesis could also explain certain thermal reactions i.e. reactions brought about by molecular collision. The authors showed how the decomposition of a gas could be brought about by collision and yet obey the unimolecular gas law. They also showed that on the basis of a chain theory explosion was possible if the total change of energy of the reaction is greater than its energy of activation.

The following theory developes the same lines as that pursued by Christiansen and Kramers. Consider a gas which we will signify by A for the sake of simplicity. Gas A can react to give another gas B. According to the theory of Arrhenius only some of the molecules of A, those which he called activated, can give B. Let the normal molecule be signified by A_n and the active molecule by A_a. The active molecule /

molecule A_a goes spontaneously to an active molecule B, B_a. When the active molecule B_a collides with A_n we get B_n and A_a formed. The new molecule A_a goes through the same process as the original one and so on. This idea is shown in the following sketch.



The latter A_a - B_a which collides with another A_n and the process repeats itself.

The rate of formation of molecules of B_n is that of the slowest of the above processes, A_a - B_a. Let the concentration of the various molecules be signified by placing square brackets round A_n etc.

$$-\frac{d[A_n]}{dt} = -\frac{d[A_a]}{dt} = \frac{1}{\tau}[A_a]$$

Rate of destruction of An (by going to Aa) | Rate of destruction of Bn (by going to Ba) | where τ = mean free life of Aa

If the reaction is a stable one i.e. If the rate of the reaction does not vary with time then

$$\frac{d[A_a]}{dt} = 0 \quad \text{and} \quad \frac{d[B_a]}{dt} = 0$$

<u>The active molecule Aa is formed.</u>

(1) Thermally, by a collision between two molecules when the relative energy of these molecules exceeds the energy of activation E. The probability of this is $Ze^{-\frac{E}{RT}}$ where Z is the total number of collisions. The rate of this reaction by the mass

action law = $q[An]^2$ (q is a constant).

(2) By a collision between B_a and A_n.

Rate = $\alpha r[B][A_n]$

r = collision number

α = the probability that a collision of this kind leads to activation.

The active molecule A_a is destroyed.

(1) By spontaneous change into B_a

Rate = $s[A_a]$

(2) By collision with An.

Rate = $t[A_n][A_a]$

where s and t are constants

B_n is assumed to be small and therefore its corresponding collisions are neglected.

$$0 = \frac{d[A_a]}{dt} = q[A_n]^2 + \alpha r[B_a][A_n] - s[A_a] - t[A_n][A_a] \quad \cdots (1)$$

Similarly

$$0 = \frac{d[B_a]}{dt} = s[A_a] - r[B_a][A_n] \quad \cdots (2)$$

$$\text{or } [B_a] = \frac{s[A_a]}{r[A_n]} \quad \cdots (3)$$

substituting (3) in (1)

$$[A_a] = \frac{q[A_n]^2}{s(1-\alpha) + t[A_n]}$$

$$-\frac{d[A_a]}{dt} = \frac{1}{\tau} \frac{q[A_n]^2}{s(1-\alpha) + t[A_n]}$$

If every collision between B_a and An leads to formation of one molecule A_a (i.e. $\alpha = 1$) then

$$-\frac{d[A_a]}{dt} = \frac{1}{\tau} \frac{q}{t}[A_n]$$

This means that the rate of the reaction is <u>proportional to the concentration</u> of the gas although the reaction is brought about by collision.

The limiting condition for very great velocity of reaction i.e. for "explosion" is

$$\frac{d\left[A_a\right]}{dt} = \infty \qquad \text{i.e. that}$$

$$t\left[A_n\right] + \nu\,(1-\alpha)s = 0$$

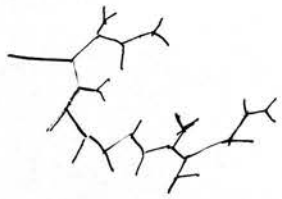
This equations is only possible if α is greater than 1 as t, s, and A_n are all positive values. α can exceed 1 in two ways. B_a might have sufficient energy to activate two molecules either in a termolecular collision or in two separate collisions.

The above theory gives as the chain propagators activated molecules, but a more satisfactory theory results if we assume that the chain propagators are atoms or radicals. Let us suppose that we have a diatomic molecule A_2, and that the atoms of this molecule can unite with a molecule B to give AB. The following scheme shows the mechanism of the reaction.

$$\begin{array}{ccccccc} AB' & \xleftarrow{+B} & A & \leftarrow & A_2 & \rightarrow & A \xrightarrow{+B} AB' \\ \downarrow{\scriptstyle +A_2} & & & & & & \downarrow{\scriptstyle +A_2} \\ \leftarrow A+AB+A\rightarrow & & \text{e.t.c.} & & & & \leftarrow A+AB+A\rightarrow \end{array}$$

The activation of A_2 is in this case dissociation into two atoms of A. These atoms react with B to give AB with a high content of energy. The energetic AB on colliding with A_2 loses its energy by dissociating A_2 into its atoms. It can therefore be seen that /

every atom of A, therefore the chain branches as shown below.



It might be concluded from the above that an exlosive reaction has branching chains.

A more complete treatment of chain branching has been given by Semenoff[4] who reasons in the following manner.

Let n be the total number of <u>activated</u> molecules present, therefore the number of molecules reacting is n so that the rate of the reaction may be put = n. Let the total number of collisions between <u>all</u> the molecules in unit time = Z. Activation only occurs when the energy of the colliding molecules exceed a certain value E. The probability of this is

$$\text{Rate of the Reaction} = n = Ze^{-\frac{E}{RT}}$$

This is not correct when <u>secondary</u> activation takes place. Each elementary reaction gives up an amount of energy E + Q, where Q is the heat of the reaction, and this energy must be distributed as potential and kinetic energy among the molecules. Suppose that each of the molecules formed in the reaction possess a fraction φ of E + Q. This molecule with energy φ on colliding with another molecule of the gas whose energy exceeds E - φ will lead to activation. The probability of this /

this collision occurring $e^{-\frac{E-\epsilon}{RT}}$ i.e. each primary process a_o, leads to a secondary process $a = a_o e^{-\frac{E-\epsilon}{RT}}$

The rate of the reactione is therefore

$R = n + \alpha R$

Due to primary activation; Due to secondary activation

α is the probability of secondary activation.

$$R = \frac{n}{1-\alpha}$$

If $\alpha = 1$ the reaction gives an infinite chain

If $\alpha < 1$ the number of links of the chain for one primary reaction $= \frac{1}{1-\alpha}$

If $\alpha > 1$ the reaction gives branching chains and explosion occurs.

Let the concrete example of the $H_2 : Cl_2$ reaction now be examined(5)

$Cl_2 = Cl + Cl - 56000$ cal --- --- (1)

$Cl + H_2 = HCl + H + 0$ cal.--- --- (2)

$H + Cl_2 = HCl + Cl + 45000$ cal. --- (3)

$Cl + H_2 = HCl + H$ --- --- --- (4)

The above equations (1) (2) (3) and (4) show how a straight reaction chain can take place, but does not show the possibility of chain branching. The energy of reaction (3) is given up as kinetic energy say to $\vec{HCl}$ and $\vec{Cl}$ equally. If one of these energetic molecules collides with a molecule of Cl_2 whose /

whose energy content consists of U = 56000 - 23000 = 33000 cal., Cl_2 splits into two atoms which form two new starting points for the chain. The probability of this branching occurring =

$$\frac{[Cl_2]}{[H_2]+[Cl_2]}\, e^{-\frac{U}{RT}} = \delta \qquad (5)$$

If this branching is not taken into consideration then the reaction velocity $R' = n_0 \nu$, where n_0 is the number of atoms formed in unit time by (1) and ν is the number of elementary reactions given by the Nernst Chain. The presence of the secondary activation (or of the chain branches) accelerates the rate of the reaction so that

$$R = n_0 \nu + \nu \delta R$$

$$R = \frac{n_0 \nu}{1 - \nu \delta} = \frac{n_0 \nu}{1 - \frac{\nu [Cl_2]}{[H_2]+[Cl_2]} e^{-\frac{U}{RT}}} \qquad (6)$$

At low temperatures where $e^{-\frac{U}{RT}} \ll 1$, R = R approx. At higher temperatures S approaches 1 and greatly influences the rate of the reaction. When $\nu\delta = 1$ $R = \infty$.

The condition for "explosion" is

$$\nu \delta = \nu \frac{[Cl_2]}{[H_2]+[Cl_2]} e^{-\frac{U}{RT}} = 1 \qquad (7)$$

If we assume that the chain is broken in the gas phase by traces of O_2 we get.

$$\nu = \frac{1}{x_1 \frac{[O_2]}{[H_2]} + x_2 \frac{[O_2]}{[Cl_2]}} = \frac{[H_2][Cl_2]}{\{x_2[H_2] + x_1[Cl_2]\} O_2} \qquad (8)$$

If the chain is broken at the wall then

$$\nu = \frac{3\pi x^2}{2\lambda_0^2} [H_2][Cl_2] \qquad (9)$$

(where x = the linear dimensions of the vessel,

λ_o = the mean free path at unit pressure,

$[\lambda_o^2$ at 1 mm. Hg. = $6.10^{-9}]$)

Equation (9) is derived as follows.

The number of collisions of a particle going through a gas a distance $x = \frac{3\pi}{4} \frac{x^2}{\lambda^2}$ where λ is the mean free path.

The chain propagators are H and Cl atoms. Let n be the total number of collisions undergone by the atoms. Four different kinds of collisions are suffered by these particles 1, $H + H_2$.
2. $H + Cl_2$. 3 $Cl + H_2$ 4. $Cl + Cl_2$.
A reaction only takes place during the collisions of type 2. and 3. Let n_1 be the number of collisions of type 1. and 2, n_2 be the number of collisions of type 3. and 4., ν_1 the number of collisions of type 1, and ν_2 the number of collisions of type 3. On the assumption that the diameter of all the particles are equal, we have the following equations.

$\nu_1 = \nu_2$ (1) $n_1 + n_2 = n$ (2)

$$\therefore \nu_1 = \frac{[Cl_2]}{[H_2]+[Cl_2]} n_1 \quad (3) \text{ and } \nu_2 = \frac{[H_2]}{[H_2]+[Cl_2]} n_2 \quad (4)$$

$$\therefore \nu_1 = \frac{[Cl_2]}{[H_2]+[Cl_2]} n - \frac{[Cl_2]}{[H_2]+[Cl_2]} n_2 \quad ---- \quad (5)$$

Substituting for n_2, $\frac{[H_2]+[Cl_2]}{[H_2]} \nu_1$ which is given by (4) and (1), in (5) we get

$$\nu_1 = \frac{\frac{[Cl_2]}{[H_2]+[Cl_2]} n}{1 + \frac{[Cl_2]}{[H_2]}} = \frac{[H_2][Cl_2]}{([H_2]+[Cl_2])^2} n = [H_2][Cl_2] \frac{3\pi x^2}{4\lambda_o^2}$$

Now total number of links of chain =

$$\nu = \nu_1 + \nu_2 = \frac{6\pi^2\chi^2}{4\lambda_0^2}[H_2][Cl_2]$$

If we let p = pressure of the mixture of H_2 and Cl_2 and γp = pressure of Cl_2 therefore $(1-\gamma)p$ = pressure of H_2 substituting these values in equations (8) and (9) above and then applying the condition for explosion (7) we get

$\log p = \left(\frac{U}{RT}\right) + C_1$ (8′) and $\log p = \left(\frac{U}{2RT}\right) + C_2$ (9′)

These equations show the effect of temperature on the "explosion" pressure.

A simple way of finding the condition of explos-:ion assuming that the chains are broken in the gas phase and at the wall has been given by Hinshelwood and Thompson[6].

Let a = of the active molecules of reactant
and a′ = " " " " product.

$$\frac{da'}{dt} = f_0(c) - f_1(c)a' + \alpha f_2(c)a - f_s a - f_c a'$$

Rate of formation of a′	Production by spontaneous reaction	Loss by deactivation of product by reactant which takes the energy	Production from activated molecules of reactant by reaction	Deactivation by surface	Deactivation in the gas phase
	(1)	(2)	(3)	(4)	(5)

$$\frac{da}{dt} = f_1(c)\, a - f_2(c)\, a$$

Production from activated product (process (2))

Loss by chemical reaction of activated reactant molecules, which produce activated molecules of product in (3)

$f_o(c)$, $f_1(c)$, $f_2(c)$ and f_c are functions of concentration, f_s of surface and of concentration.

For a stationary reaction i.e. a reaction which goes with stable velocity

$$\frac{da'}{dt} = \frac{da}{dt} = 0$$

Solving the equations we get Rate of the reaction $= f_2(c)\, a = \dfrac{f_o(c)\, f_1(c)}{f_s + f_c + (1-\alpha) f_1(c)}$

---

or we can write

$$\text{Rate} = \frac{F(c)}{f(c,s) + A(1-\alpha)}$$

---

where $f(c,s)$ is the amount of deactivation by surface and in the gas phase.

The condition for "explosion" is $f(c,s) + A(1-\alpha) = 0$

This equation shows clearly that the amount of branching required to give "explosion" depends on the efficiency of the gas and of the surface in breaking the chains.

Criteria of a chain reaction.

(1b The rate of the reaction depends on the size of the vessel, the concentration of the reacting gases and on the concentration of foreign gases.

(2) The reaction is explosive over a certain range of pressure and the explosion limits depend on the nature and size of the reaction vessel and on the pressure of the foreign gas at a given temperature.

We will now consider Semenoff's Theory [7] of combustion processes in detail.

As has already been stated a reaction can only take place between activated molecules.

(number of activated molecules $n_{A'} = n_A e^{-\frac{E}{kt}}$)

Let the unit of volume of the active molecule A' and the normal molecules A and B be signified by a', a and b respectively. The velocity of the reaction depends on the number of collisions between the molecules A' and B. i.e. velocity

$W = \sqrt{2}\,\pi\sigma^2\bar{u}\,b\,a' = z\,a\,b\,e^{-\frac{\varepsilon}{RT}}$

where σ = molecular diameter and $\bar{u}$ = the velocity of the molecules.

The primary reaction as has already been shown often produces energy which can excite the reaction mixture, and a chain reaction results. "Explosion" can take place (1) because of <u>energy</u> chains set up by the kinetic energy of the molecules (2) because we /

we have molecules which are activated to give some kind of excited state e.g. P_4 in O_2 and S_8 in O_2

Consider a mixture of two molecules A and B. Suppose that, when reaction takes place, Q calories are formed per mol. The quantity of heat developed per sec.

$$= q_1 = \frac{QW}{N} V = \frac{z\,Q\,a\,b}{N} e^{-\frac{E}{RT}} V = \frac{A}{N} e^{-\frac{E}{RT}} a\,b\,V$$

$$= B\, e^{-\frac{E}{RT}} a\,b$$

where N = Avagadro's number

V = the volume of the vessel

If the wall of the vessel is at a temperature T_o the quantity of heat given away per second by the wall is at a first approximation $= q_2 = x\,(T - T_o)$ where x is a constant.

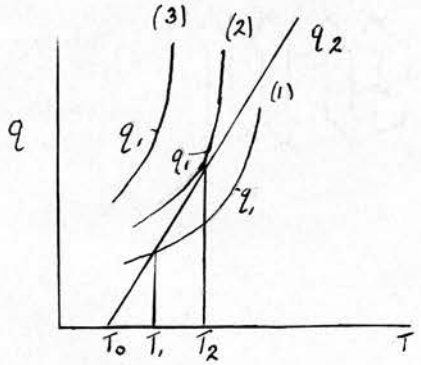


Fig. 1.

In Fig. 1. the relation of q_2 to the (1) (2) and (3) q_1 curves, which show different values for the heat of the reaction of a and b, is given. Let curve (1). be examined and let the temperature of the gases on entering the vessel be equal to T_o. At this moment $q_1 > q_2$ and therefore the gas heats up in consequence of the reaction until $q_1 = q_2$.

A /

A further change in the temperature is now impossible and the reaction goes at a temperature T_1 according to the formula of Arrhenius. Let curve (3) now be examined. In this case the q_1 curve lies above the q_2 curve and the heating therefore increases with time, and "explosion" occurs. The process in the sphere of a stationary reaction is shown in curve (2), it touches the q_2 line in a point. This is given by the following relations

$$q_1 (T_2) = q_2 (T_2) \quad , \quad \left(\frac{dq_1}{dT}\right)_{T_2} = \left(\frac{dq_2}{dT}\right)_{T_2}$$

$$\text{or } Bab e^{-\frac{E}{RT_2}} = \chi (T_2 - T_0) \quad \ldots \quad \ldots \quad (1)$$

$$\text{and } Bab e^{-\frac{E}{RT_2}} = \frac{\chi R T_2^2}{E} \quad \ldots \quad \ldots \quad (2)$$

$$T_2 = \frac{E}{2R}\left(1 - \sqrt{1 - \frac{4RT_0}{E}}\right)$$

Making an approximation, which according to H.A. Taylor [8], is hardly justifiable, we get

$$T_2 = T_0 \left(1 - \frac{RT_0}{E}\right)$$

Placing this in (2) we get

$$Bab e^{-\frac{E}{RT_0}+1} = \frac{\chi R T_0^2}{E} = 2.8\, Bab e^{-\frac{E}{RT_0}}$$

If n = the total number of molecules of the mixture and a = yn, $\therefore$ b = (1-y) n we get

$$2.8B(1-y)yn^2 e^{-\frac{E}{RT_0}} = \chi \frac{RT_0^2}{E}$$

If $n = \frac{n_0 \delta}{\delta_0}$ where n_0 and δ_0 = the number of molecules and their density at N.T.P. respectively.

$$\therefore \chi \frac{RT_0^2}{E} = n_0^2\, 2.8\, B (1-y)\, y \left(\frac{\delta}{\delta_0}\right)^2 e^{-\frac{E}{RT_0}}$$

$$= C\left(\frac{\delta}{\delta_0}\right)^2 e^{-\frac{E}{RT_0}}$$

where C is a constant for the combination

This formula shows that there is a critical density above which explosion can occur, and that for <u>each density</u> there can be a <u>wall temperature</u> above which explosion is possible.

The above formula can be put in the form

$$\log\left(\frac{S}{T_o S_o}\right) = -\frac{1}{2}\frac{E}{RT}\log e - \frac{1}{2}\log C$$

$$\text{or } \log\left(\frac{p}{T}\right) = \frac{A}{T} + B \qquad A = .09E^{(8)}$$

Sagulin has investigated a number of reactions and finds that when $\log\left(\frac{p}{T}\right)$ is plotted against $\frac{A}{T} + B$ a straight line is obtained.

It has already been stated that we have a certain range of pressure in which "explosion" can occur. Now at the lower limit of this pressure the chains must be principally broken at the walls since lowering of the pressure <u>reduces</u> the number of gas collisions. This lower limit will now be examined.

For clarity the concrete example of the oxidation of phosphorus will be taken but the proof is a general one.

Let the chain propagators be X_o and X_p and suppose X_o is produced spontaneously at a rate $k_1 F(c)$ and that

X_o collides with p_4 to give X_p

X_p " " O_2 " " X_o

As before for the stationary chains we have.

$$\frac{d p_{X_o}}{dt} = k_1 F(c) + \alpha k_2 p_{X_p} p_{O_2} - k_3 p_{X_o} p_{P_4} - K p_{X_o} = 0 \cdots (1)$$

(Rate at which X_o is destroyed at walls.)

and

$$\frac{d p_{X_p}}{dt} = k_3 p_{X_0} p_{P_4} - k_2 p_{X_p} p_{O_2} - K p_{X_p} = 0 \text{ - - - - - (2)}$$

$$\therefore k_1 F(c) + (\alpha - 1) k_2 p_{X_p} p_{O_2} - K p_{X_p} = 0 \text{ - - - - - - (3)}$$

from (2)

$$p_{X_p} = \frac{k_3 p_{X_0} p_{P_4}}{k_2 p_{O_2} + K}$$

substituting in (3)

$$k_1 F(c) + \frac{k_2 k_3 (\alpha - 1) p_{X_0} p_{P_4} p_{O_2}}{k_2 p_{O_2} + K} - K p_{X_0} - \frac{K k_3 p_{X_0} p_{P_4}}{k_2 p_{O_2} + K} = 0$$

$$\therefore k_1 F(c)(k_2 p_{O_2} + K) + k_2 k_3 (\alpha - 1) p_{X_0} p_{P_4} p_{O_2} - K p_{X_0} (k_2 p_{O_2} + K) - K k_3 p_{X_0} p_{P_4} = 0$$

$$\therefore p_{X_0} = \frac{-k_1 F(c)(k_2 p_{O_2} + K)}{k_2 k_3 (\alpha - 1) p_{P_4} p_{O_2} - K k_2 p_{O_2} - K^2 - K k_3 p_{P_4}}$$

For on "explosion"

$$p_{X_0} = \infty$$

$$\therefore k_3 (\alpha - 1) p_{P_4} p_{O_2} - K p_{O_2} - \frac{K^2}{k^2} - K \frac{k_3}{k_2} p_{P_4} = 0$$

$$\therefore (\alpha - 1) k_3 p_{P_4} p_{O_2} = K (p_{O_2} + p_{P_4}) + \frac{K^2}{k_2} \text{ - - - - (4)}$$

Now the time required for a molecule to go a distance x from its original position is given by the equation $x^2 = 2Dt$ where D is the diffusion coefficient, and t the time.

The rate at which propagators will be destroyed at the wall

$$= K \sim \frac{1}{t} \sim \frac{2D}{x^2}$$

If /

If we suppose that the masses and diameters are equal $D \sim \frac{1}{\text{Total Pressure}}$.

$$K = \frac{k_2}{x^2 (p_{p4} + p_{o_2} + p_x)}$$ (p_x is the pressure of foreign gas)

Substituting this value in equation (4) and assuming $k_3 = k_2$ and that $\left(\frac{K^2}{k_2 k_3}\right)$ is small we get

$$p_{o_2} p_{p_4} \left(1 + \frac{p_x}{p_{o_2} + p_{p_4}}\right) = \text{constant} \quad \ldots \quad (5)$$

One further point, however, needs consideration. The above calculation makes the unwarrantable assumption that the masses and diameters of all the molecules are equal. To introduce the necessary correction let us consider that a single molecule is diffusing through a ternary gas, and that the diffusion coefficients are D_1 D_2 and D_3 and assume that $t \sim \frac{1}{D_1} + \frac{1}{D_2} + \frac{1}{D_3}$

Now $D \sim \frac{1}{M^{\frac{1}{2}} p \sigma^2}$ where M = molecular weight

p = pressure

σ = molecular diameter

$$K \sim \frac{1}{\frac{1}{D_1} + \frac{1}{D_2} + \frac{1}{D_3}} \sim \left(M_1^{\frac{1}{2}} p_1 \sigma_1^2 + M_2^{\frac{1}{2}} p_2 \sigma_2^2 + M_3^{\frac{1}{2}} p_3 \sigma_3^2\right)^{-1}$$

Now let $\sigma_1 = \sigma_2$ and $M_1 = M_2$ as these are constants /

constants for any particular reaction then

$$K \sim \left(p_1 + p_2 + \frac{\sigma_3^2 M_3^{\frac{1}{2}}}{\sigma_1^2 M_1^{\frac{1}{2}}} p_3\right)^{-1}$$

Substituting this value in (4) we get

$$p_{P_4} p_{O_2} \left(1 + \frac{\sigma_3^2 M_3^{\frac{1}{2}}}{\sigma_1^2 M_1^{\frac{1}{2}}} \frac{p_x}{p_{P_4} + p_{O_2}}\right) = \text{constant}$$

now substituting $\sigma_1^2 M_1^{\frac{1}{2}} = k$ and putting for $\sigma_3^2 M_3^{\frac{1}{2}}$,

$$\sigma_{Ax}^2 \left(\frac{1}{M_A} + \frac{1}{M_x}\right)^{-\frac{1}{2}}$$ where M_A and M_X are the molecular weights of the diffusing molecules and of X, the equation finally becomes

$$p_{P_4} p_{O_2} \left(1 + \frac{\sigma_{Ax}^2 \left(\frac{1}{M_A} + \frac{1}{M_x}\right)^{-\frac{1}{2}}}{k} \frac{p_x}{p_{P_4} + p_{O_2}}\right) = \text{Constant} \quad (6)$$

This equation was worked out quite recently by Melville. (9)

Experimental Evidence of Chain Reaction.

Many gaseous reactions have recently been shown to be explained on the above chain theories. The best examples are the oxidation of phosphorus vapour, of hydrogen, of carbon disulphide, of hydrogen sulphide, of certain simple organic compounds and of sulphur. The oxidation of phosphorus was studied by Chariton and Walta[10], Semenoff[11] and Kowalski[12], and it was established that the luminescent oxidation only took place between two pressure limits of reacting oxygen - the lower and upper critical oxidation limits. Below the lower limit no reaction could be observed at all while it was shown by Lord Rayleigh[13] that above the upper limit the reaction was very slow. These observations are in accordance with the theory of a chain reaction and Semenoff found that the lower oxidation limit was given by the equation

$$p_{P_4}^{\frac{1}{2}} p_{O_2}\left(1 + \frac{p_x}{p_{O_2} + p_{P_4}}\right) d^2 = \text{constant}$$

where p_{P_4}, p_{O_2} and p_x are the pressure of phosphorus vapour, oxygen and of inert gas at the lower limit and d is the diameter of a cylindrical reaction vessel. This is in agreement with the theory although the factor $p_{P_4}^{\frac{1}{2}}$ instead of p_{P_4} has not yet been accounted for. Dalton and Hinshelwood[14] examined /

examined the lower explosion limit of phosphine and found that a similar equation held. Recently Melville and Ludlam[15] have investigated the effect of various foreign gases on the lower critical oxidation limit of phosphorus vapour and they have found that when p_{P_4} is kept constant and $\frac{1}{p_{O_2}}$ is plotted against $1 + \frac{p_x}{p_{O_2} + p_{P_4}}$ straight lines are obtained. The slopes of these lines vary with the nature of the foreign gas.

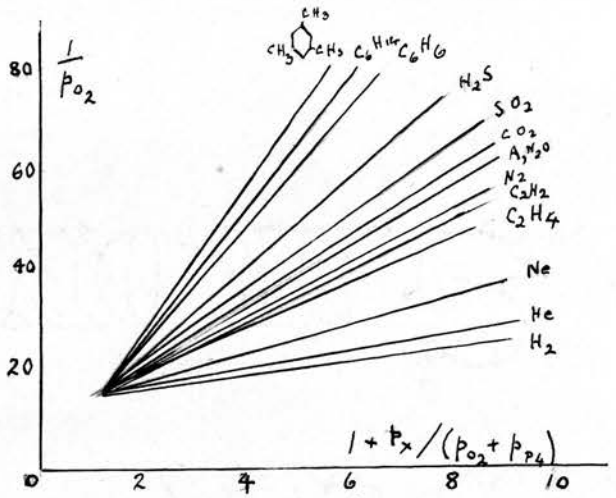


Fig 2

As can be seen from Fig. 2 the simplest gas gives the smallest slope i.e. it effects the reaction least. This result is explained by the fact that Semenoff's equation is deduced by assuming that the molecular diameters and masses of all the gases present are equal and it is therefore only a first approximation. A second approximation (see page 17) which takes into consideration the differences of these physical properties shows that the most complicated gases have the greatest effect in reducing the pressure of phosphorus vapour and oxygen required /

required for explosion to take place.

Hinshelwood,[16] Thompson[6] and other workers at Oxford, and Alyea and Haber[17] at Berlin have investigated the reaction between hydrogen and oxygen.

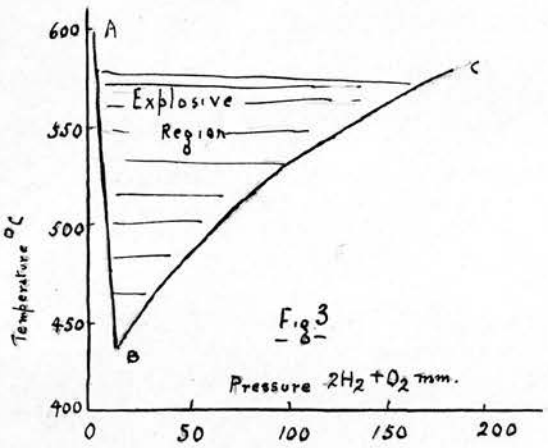


Fig 3

It has been found that 550° explosion takes place between a pressure of 10mm. and 100mm. (see fig.3) The upper pressure limit was independent of the size of the vessel showing that the most important deactivation was taking place in the gas phase.

Above the upper limit a reaction proceeds at a measurable velocity and this is shown to be chain reaction, by the fact that the velocity is <u>decreased</u> by <u>increasing</u> the surface of the containing vessel and is very much increased by the presence of foreign gas. This shows that the chain is principally <u>broken</u> at the surface, the inert gases impeding the chain propagators reaching the walls. Alyea and Haber mixed hydrogen and oxygen ~~and~~ at 550° without the presence of a "wall" and obtained no explosion. This experiment was effected by crossing streams /

streams of hydrogen and of oxygen ~~to~~ at right angles to each other in a space filled with nitrogen This experiment if reliable (Thompson[18] has recently thrown some doubt on this) is very conclusive evidence that the chain is <u>initiated</u> by the surface of the containing vessel. It has been shown[19] that the presence of nitrogen peroxide in a hydrogen oxygen mixture which normally only reacts slowly <u>initiates</u> an explosive reaction. This is explained by the fact that the peroxide reacts with hydrogen to give a chain propagator. Thompson[20] has very recently studied the effect of inert gases on the lower explosion limit of hydrogen oxygen mixtures, when the explosion is initiated by a spark.

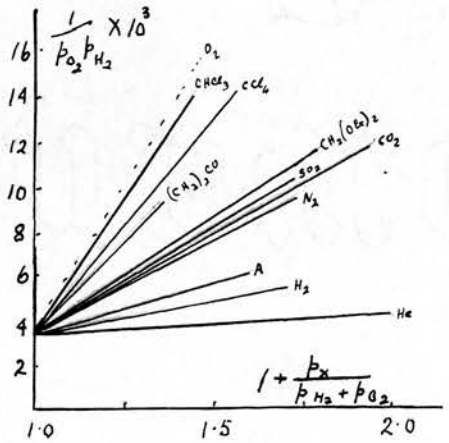


Fig 4

He finds that the presence of foreign gases lowers the critical explosion pressure of hydrogen and oxygen in the same order as found for the oxidation of phosphorus vapour (see fig. 4)

The /

The oxidation of hydrogen sulphide has been studied by Thompson and Kelland.[21] Ignition takes place at a temperature of 220-300° . When $\log\left(\frac{p_m}{T}\right)$ is plotted against $\frac{1}{T}$ where p_m is the minimum ignition pressure at a temperature T a straight line is obtained in accordance with the theory already given (see page 15). At a temperature below the explosion temperature a measurable reaction takes place and this is shown to be a chain reaction by the fact that <u>increasing</u> the surface <u>decreases</u> the rate of the reaction. The reaction is retarded by increasing the pressure of hydrogen sulphide and by adding nitrogen, but is accelerated by increasing the pressure of oxygen. That hydrogen sulphide inhibits the reaction is demonstrated by the phenomena of "successive explosions". After explosion has taken place the reaction continues at a measurable rate until the proportion of oxygen has increased to a certain value when another explosion takes place and so on. The reaction or the explosion is always preceded by an induction period which varies with the pressure, temperature and composition of the mixture. It is shortened by increasing the proportion of oxygen and lengthened by increasing that of hydrogen sulphide. Nitrogen is also found to lengthen the induction period and to a greater extent as the pressure increases./

increases. It would appear that during the induction period active centres are being formed which can start a chain reaction.

Thompson[22] has found that carbon disulphide and oxygen ignite between two pressure limits at a temperature about 140°

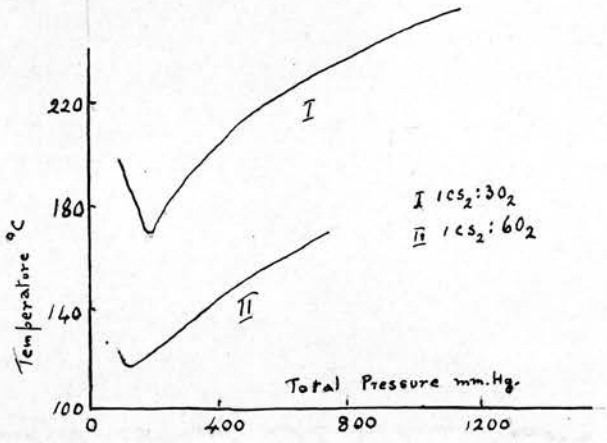


Fig. 5.

An experiment conducted without the presence of a wall (using the same method as that used by Alyea and Haber for the $H_2:O_2$ reaction) shows that the explosion temperature is much higher for the same pressure. The range of explosion pressure widens with rise of temperature as shown in Fig. 5. Increasing the proportion of oxygen favours explosion, while increasing the proportion of carbon disulphide retards explosion. Bromine, and ethylene raise the lower pressure limit, while nitrogen has little effect. The presence of these gases do not affect the upper pressure limit much unless their concentration is very high. Apparently ethylene, bromine and carbon disulphide break the chain by chemical reaction /

reaction with the chain propagator. It is suggested that the walls break the chains because they are covered with absorbed carbon disulphide. Sagulin has investigated the effect of temperature on the explosion limit and has found that the relation $\log \frac{p_m}{T} = \frac{A}{T} + B$ (p_m = lower limit of pressure) holds for the $CS_2:3O_2$ explosion as well as for the explosions $CO:O$, $H_2:Cl_2$, $CH_4:O_2$ and others.

Very recently Thompson and Kearton (23) have investigated the effect of foreign gases on the lower critical oxidation limit of the "explosive" methane oxidation, when the explosion is initiated by means of a spark.

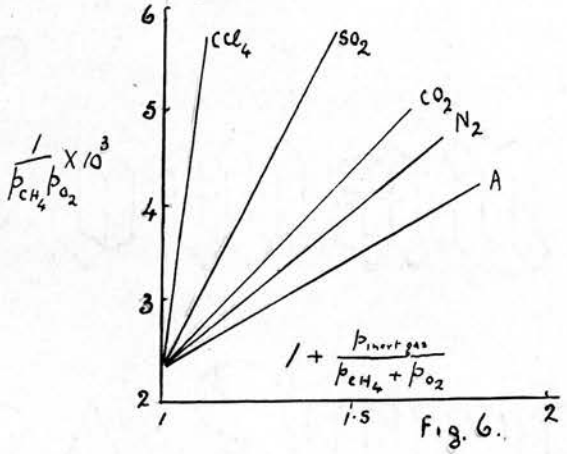


Fig. 6.

As is shown in Fig. 6, the result obtained is similar to that of the corresponding $H_2:O_2$ explosion and is further evidence that the condition for explosion depends on the rate of diffusion of the chain propagators to the walls of the vessel.

It may be mentioned here that if one calculates /

calculates the value of the fD_x^{-1} which has to be multiplied by p_x (pressure of inert gas) so that

$$p_{CH_4} p_{O_2} \left(1 + \frac{fD_x^{-1} p_x}{p_{CH_4} + p_{O_2}}\right) = \text{constant}$$

it is found that the values are generally much lower than the corresponding values for the $H_2:O_2$ "explosion". This appears to show that the chain propagators of the $H_2:O_2$ explosion are much smaller than that of the $CH_4:O_2$ explosion. The obvious suggestion to explain this is that the chain propagator of $H_2:O_2$ explosion are hydrogen atoms.

(It may be mentioned here that Thompson is apparently in error in assigning an inert gas effect to H_2 and to O_2 as the effects of these gases are already taken account of in the equation, see page 15)

The above experiments show that explosion occurs when we have <u>effective</u> chain branching. The active centres necessary to initiate an explosion may be present at ordinary temperatures, may be formed at high temperatures, may be formed by a spark, or may be formed when a foreign substance is introduced.

Part 11.

The Oxidation of Sulphur.

The Oxidation of Sulphur Vapour.

Summary of Previous Investigations.

Sulphur burns in normal pressures of oxygen to give sulphur dioxide, when it is heated to 285°C. Bodenstein and Caro [24] studied the slow oxidation of sulphur and came to the conclusion that the reaction was confined to the surface, that it varied with the oxygen pressure and that the reaction had a high temperature coefficient. Norrish and Rideal [25] carried out a more thorough examination of the reaction using oxygen pressures of .1 to 1 atmosphere and temperatures from 235° to 385°C. A steady stream of oxygen was passed through bulbs containing sulphur and the sulphur dioxide formed was analysed by passing it into a known volume of standard iodine solution. These authors found that the reaction velocity was proportional to the sum of the area of the walls of the vessel and the area of the surface of the liquid sulphur. They therefore concluded that the reaction takes place on a film of liquid sulphur which completely covers the walls. Above 305°C. abnormal results were obtained due to the secondary formation of SO_3 and below 200°C. no reaction was observed. Between 235° and 305°C. they were able to divide the reaction into two surface reactions A and B. The A reaction becomes independent of pressure /

pressure at a certain value, while the B reaction is dependent on the pressure through the whole range. From the temperature coefficient of the reaction velocity they find that the apparent heat of activation of the A reaction = 25,750 calories and for the B reaction 37,450 calories. No luminescence was observed by these authors, but above a pressure of .75 atmospheres at 285° explosion occurred and a blue flame played over the surface. Sometimes this explosion occurred at lower temperatures and pressures and completely upset the equilibrium of the bulb.

A number of investigators[26] have observed that, under certain conditions, the oxidation of sulphur is accompanied by phosphorescence. passed air over molten sulphur, which is maintained at 240°C. in a shallow tray. The flame obtained in this way is much whiter than the ordinary sulphur flame and it is relatively cold. Most of the investigators state that the phosphorescent oxidation begins about 200°C. Emeléus made a study of the phosphorescent combustion chiefly to find out the reaction products. Experiments were conducted at the temperatures of 275°, 300° and of 325°C.. The combustion was controlled by passing nitrogen which contained 15 to 20% of oxygen over the sulphur. A careful examination of the reaction products showed /

showed them to be sulphur dioxide and a very small amount of sulphur trioxide. No evidence of a lower oxide was found and this agrees with the observations of Watson[26]. Emeléus in the course of his investigation discovered that certain organic vapours and sulphur dioxide inhibit the glow. He concludes that the phosphorescence of sulphur is of the same nature as the phosphorescence of phosphorus and that the reaction proceeds in the gas phase by means of active molecules.

Semenoff and Rjabinin[27] have carried out an investigation of the oxidation of sulphur for pressures from about 20mm. of mercury downwards.

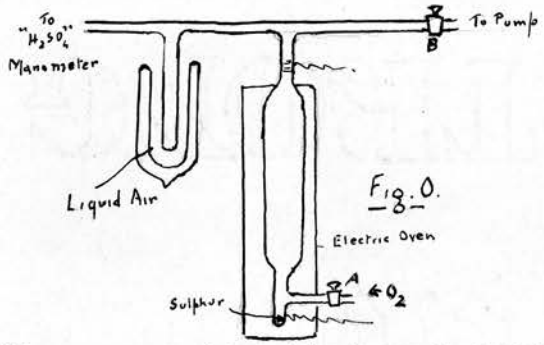


Fig. 0.

The apparatus that was used is shown diagrammatically in Fig. 0. The reaction vessel which contains the sulphur is heated by the electric oven to a temperature lying between 80° and 120°C.. Any SO_2 or SO_3 formed is immediately condensed in a side tube which is placed in liquid air. When oxygen is introduced into the apparatus no luminescence is in general observed. If a discharge is sent through the vessel for one or two seconds by means of the external electrodes /

electrodes at top and bottom a luminescent oxida-:tion is started. For oxygen pressures between .5 and 20mm. Hg the luminescence fills the whole volume and for larger pressures the luminescence is concentrated more and more at the surface of the sulphur. During the time of luminescence the pressure gradually falls owing to the removal of the products sulphur dioxide and sulphur trioxide by the liquid air. The amount of sulphur trioxide formed amounted to 20 to 60% of the total pressure of SO_2 and SO_3. It was sometimes found that if a vessel had been previously used combustion took place without the necessity of passing a discharge through the tube, even although the vessel was well evacuated between the experiments. The pressure at which this spontaneous combustion took place was generally much higher than the pressure at which combustion took place if a discharge was passed, but the value varied considerably from experiment to experiment. No reason for this peculiarity could be given. During the reaction very little heating takes place as no increase of pressure is observed. It was found that the luminescent re-:action was obtained if oxygen, through which a discharge had previously been passed, was introduced into the vessel. If a discharge was sent through the sulphur vapour alone and then oxygen introduced into /

into the vessel no luminescent reaction was observed. This is taken as evidence that the reaction is started by O_3 molecules or O atoms.

The rate of change of pressure shows that the reaction is practically independent of the pressure of oxygen down to a certain minimum pressure of oxygen where the reaction ceases. This shows that the reaction is similar to the phosphorus vapour oxidation in that it gives a residual pressure or "Restdruck". The velocity of the reaction varies from experiment to experiment and apparently depends on the rate of evaporation of the sulphur vapour. If the tube between the liquid air trap and the vessel is long and narrow so that the reaction products cannot be condensed sufficiently quickly, the reaction velocity decreases and sometimes the reaction stops altogether. This result is in agreement with the fact that Emeléus found that sulphur dioxide acted as an inhibitor of the phosphorescent combination. Experiments using static methods failed to give reproducible values for the residual pressure. To remedy this defect experiments were carried out using a streaming method. By means of tape A and B a stream of oxygen at a certain pressure was passed through the vessel. If luminescence was observed after the discharge had been passed then the pressure was above the residual /

residual pressure.("Restdruck"). The pressure of oxygen was then gradually reduced until the luminescence disappears. In order to make certain whether luminescence was present or absent tap B was shut and the pressure of oxygen was allowed to rise. If luminescence has been present before tap B was closed, then the intensity of the light would increase, but otherwise the increase of the oxygen pressure would cause no appearance of luminescence.

When the vessel was at 80°c. no luminescence was observed below a pressure of .16 mm. Hg. Luminescence was however certain at a pressure of .23 mm. Hg.

Experiments conducted using the static method give results which compare quite favourably with those obtained by the dynamic method if small pressures of oxygen are used. Oxygen was introduced into the apparatus to a pressure of about 4mm. of Hg. and tap A was then closed. No change of pressure was noticed in half an hour. A discharge was then passed through the vessel and immediately a luminescent reaction started. After 80 minutes the reaction had stopped at a pressure of .25mm. Hg. 10 minutes later oxygen was again introduced into the vessel to a pressure of about 4mm. Hg. and the discharge again passed. When the pressure in the apparatus had fallen to .5mm. Hg. oxygen was added to a pressure of 2mm. Hg. The light brightened up and /

and the reaction proceeded until a pressure of .26 mm. Hg was reached. These experiments showed conclusively that the residual pressure is due to oxygen and not to any other gas. The residual oxygen pressure was found to rise with lowering of the temperature of the reaction vessel, the following values being obtained.

$t^{\circ}C$	p_{min} (mm. Hg)
53	.28
70	.2
80	.14
90	.36?

Semenoff and Rjabinin also found that the residual pressure did not vary with the pressure of nitrogen or with the diameter of the reaction vessel.

An upper limit of oxygen pressure above which reaction could not proceed was also observed. This pressure amounted to 10mm. Hg at 53°C, 20 to 30mm. Hg at 80°C, and 60 to 90mm. Hg at 100°C.

These experiments therefore show that between certain pressure limits of oxygen luminescent oxidation of sulphur vapour can take place if we provide an active centre to start the reaction. This phenomenon can be explained on the concept of a chain mechanism, the theoretical treatment of which has already been given.

The Present Investigation.

As the above investigations were by no means complete and as recent investigations of the very similar /

similar oxidation of phosphorus had proved very fruitful in further elucidating the mechanism of a chain reaction, a further examination of the oxidation of sulphur vapour at low pressures was now conducted.

Apparatus 1.

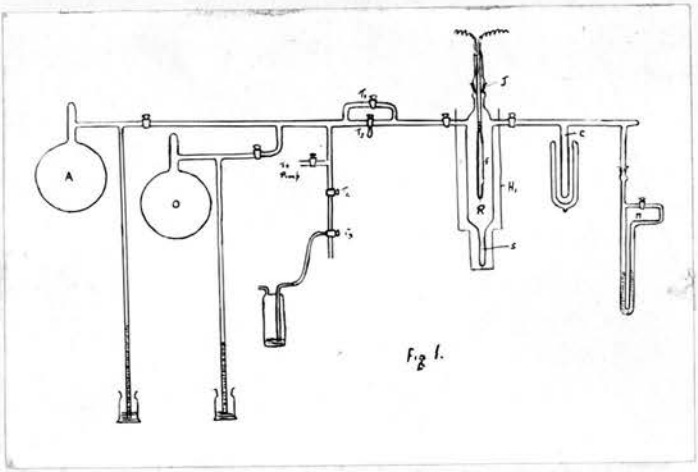


Fig 1.

The apparatus is shown diagrammatically in Fig.1 R is the reaction vessel which is made of soft glass and carries a ground joint J, so that various filaments F can be conveniently placed in the vessel. The ground joint J has a pinch seal through which runs borated wire. This is soldered to de-:gassed nickel wire, which serves as a support for the various filaments. The top part of the vessel is enclosed in an electric oven H_1, so that it can be maintained at about 120°C. The small side tube S contains the sulphur and is enclosed in a small electric oven H_3. M is a sulphuric acid manometer which is read by means of a microscope with an eye-:piece scale (1 division of the eye-piece scale corresponds to .024mm. of mercury). T_2 is a small "tap /

"tap pipette" to allow small quantities of oxygen being transferred from the oxygen reservoir O into the reaction vessel. A serves as a reservoir for other gases. C is a side tube which is placed in liquid air and which serves as a condenser for any SO_2 and SO_3 formed. The apparatus is evacuated by means of a mercury condensation pump backed by a Hyvac oil pump.

Procedure.

After evacuation O is filled with dry oxygen. The sulphur in S is purified by distilling it over to the top part of the vessel and then back to S again in vacuo. The experiment is then carried out as follows. After thorough evacuation a small quantity of oxygen is introduced into the reaction vessel by pipette T_2, tap T_1 being closed. C is placed in liquid air and H_1 and H_3 kept at 120° and 90° to 80° respectively. The filament is then heated for a certain time and the change of pressure as shown by the manometer is noticed. The temperature of the filament is kept as constant as possible by placing it in a Wheatstone Bridge so that the current can be regulated to give the filament and its leads the same resistance in a series of experiments.

RESULTS.

A. Using a Tungsten Filament.

Reaction Vessel R at 120°C. S at 95°C.

T = Time in Hours and Minutes.

R = Microscope Reading. 1 Division = .024 mm.

Z = Microscope Reading when pressure is zero.

↓ = Filament switched on.

↑ = Filament switched off.

1.

T	R
	Z =48
11.30	62.2
11.30	↓
11.40	61.2
11.50	60
12.0	59
12.	↑
12.10	58.5
12.20	58.2

2.

T	R
	Z=48
12.24	52.4
12.30	52.3
12.30	↓
12.35	52.1
12.48	51.4
1.30	50
1.30	↑

3.

T	R
	Z=48
1.35	82.3
1.40	↓
1.45	81
1.50	81.4
2.	79.2
2.10	78.3
2.15	77.7
2.20	77.0
2.26	76.3
2.30	75
2.40	74.4
2.45	74.2
2.50	74

4.

T	R
	Z=48
3.4	54.4
3.5	↓
3.10	54.1
3.16	54
3.27	53.5
3.31	53.2
3.40	53.
3.45	52.7
4.3	52.2
4.20	52

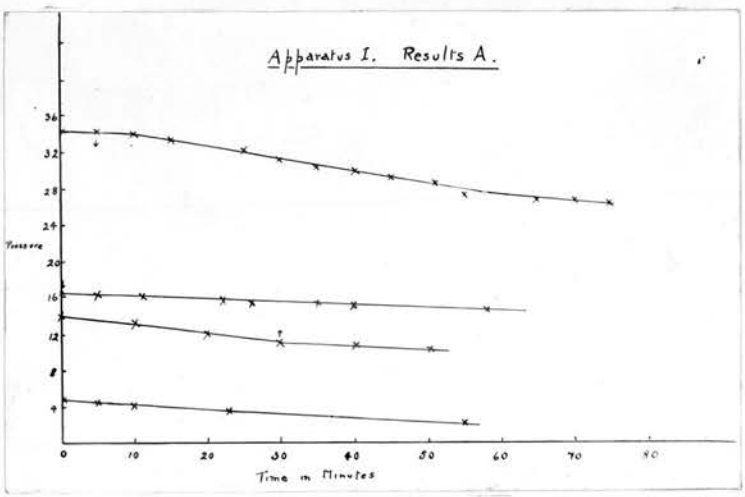


Fig. 1A

B. Using a "Pyrex" Filament.

This filament is used to prevent any misleading results which might occur due to oxidation of the tungsten filament. This filament is made by threading a pyrex capillary with Tungsten wire .1mm. in diameter. The pyrex capillary must be almost an exact fit for a satisfactory filament. This covered wire is then mounted temporarily on the nickel supports, and the pyrex melted electrically on to the wire in vacuo. The filament is then removed and pyrex cup like ends are sealed on. These cups are then filled with lead and a copper wire is embedded in it. In this way we get a filament which exposes no hot tungsten. (This type of filament was first used by Melville in connection with the oxidation of phosphorus below the lower critical oxidation limit.)

B. Using a Pyrex Filament.

Reaction Vessel R at 120°C. S at 102°C ± 4°.

1.		2.		3.		4.	
T.	R.	T.	R.	T.	R.	T.	R.
	Z=40	11	Z=40.2		Z=43		Z=42
10.55	59.2	12.10	55.9	1.55	62	2.26	61.3
11	59	12.10	↓	2.2	61.4	2.28	61.5
11.	↓	12.12	55	2.2	↓	2.30	61.5
11.4	58	12.14	51.1	2.4	60.8	2.30	↓
11.6	56.2	12.16	53	2.6	60	2.32	61
11.7	56	12.18	52.2	2.8	58.8	2.34	60.1
11.8	↑	12.20	51.2	2.10	57.4	2.36	59.2
11.10	55	12.22	50.2	2.10	↑	2.38	58.2
11.15	54.2	12.22	↑	2.12	57	2.38	↑
11.20	54	12.24	50	2.14	57	2.40	57.7

1.

T	R
11.20	↓
11.22	53
11.24	52.2
11.26	51.2
11.28	50.1
11.30	49
11.32	48
11.34	47
11.35	46.5
11.40	44.3
11.43	43.3
11.47	43

2.

T	R
12.26	49.5
12.28	49.4
12.28	↓
12.30	49
12.32	48
12.34	47
12.36	46.8
12.38	46.8

3.

T	R
2.16	56.8

4.

T	R
2.42	57.2
2.44	57.1
2.45	↓
2.47	56.2
2.49	55
2.51	54.2
2.53	53.2
2.55	52.4
2.57	51.6
2.59	50.6
3.1	49.5
3.3	48.4
3.5	47.9 ↑
3.7	47.3
3.9	47.1
3.11	47
3.11	↓
3.13	46.5
3.15	45.7
3.17	45.2
3.19	44.8
3.21	44.4
3.23	44.2
3.25	44.2

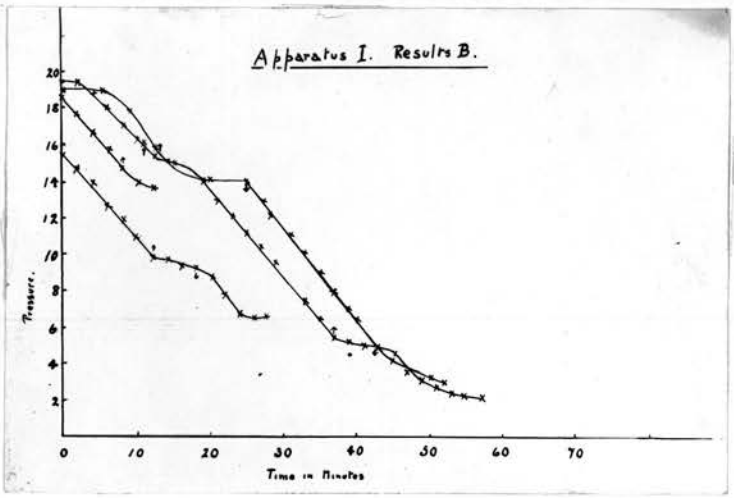


Fig 1 B

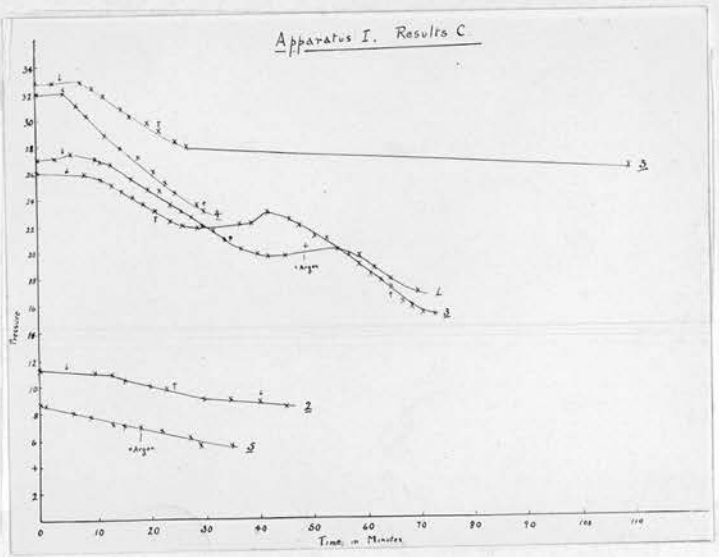

Apparatus I. Results C
Pressure
Time in Minutes
0
10
20
30
40
50
60
70
80
90
100
110
+Argon
+Argon
1
2
3
4
5

Fig. 1.C.

C. Further Results using a Pyrex Filament at a slightly different temperature.

Reaction Vessel R at 120° S at 90° ± 4°C

1.

T	R
	Z=48.3
3.25	75.5
3.28	75.5
3.29	↓
3.31	75.9
3.35	75.5
3.36	75.2
3.38	75
3.42	74
3.45	73.2
3.47	73
3.49	72
3.51	71.5
~~3.51~~	~~71.5~~
3.53	71
3.55	70.3
3.57	70
3.59	69.3
4.0	↑
4.2	68.5
4.5	68.2
4.7	68
4.10	68
2.2mm.Hg. pressure of Argon added. Microscope shifted .6	
4.10	93
4.24	↓
4.30	94
4.34	93
4.37	92
4.40	91.2
4.45	90.2

2.

T	R
	Z=43
4.56	54.3
5	↓
5.5	54.1
5.8	53.9
5.10	53.5
5.15	53.0
5.18	52.8
5.20	↑
5.25	52
5.30	52
Argon added	
5.30	64.2
5.35	↓
5.42	64.2
5.50	64

3.

T	R
	Z=40.9
12.5	41
12.7	74
12.10	74
12.11	↓
12.14	74
12.18	74
12,20	73.5
12.22	73
12.25	72
12.27	71.5
12.30	70.9
12.32	70.2
12.32	↑
12.35	69.5
12.37	69
2.0	67.2
2.1	↓
2.8	67
2.11	66.7
2.13	66.2
2.15	65.8
2.17	65.2
2.19	64.8
2.21	64.2
2.21	↑
2.22	64
2.24	63.5
2.26	63.2
2.29	63
2.31	63
Argon added	
2.35	79
2.37	79.2
2.39	79.3
2.40	↓
2.42	80
2.46	79.5
2.48	79
2.51	78.2
2.53	78
2.55	77.2
2.57	76.8
2.59	76
3.1	75.2
3.3	74.8
3.5	74.2
3.5	↑
3.7	73.2
3.9	73.8
3.11	72.4
3.13	72.2

4.

T	R
	Z=41.2
3.24	73.5
3.30	73.5
3.30	↓
3.35	73.5
3.37	72.5
3.39	71.6
3.42	70.2
3.45	69.2
3.48	68.2
3.51	67.2
3.53	66.5
3.55	65.8
3.59	64.8
4.	64.2
4	↑
4.11	63

5.

T	R
	Z=41.2
4.19	50
4.25	50
4.26	↓
4.28	49.8
4.31	49.2
4.34	49
4.38	48.5
4.40	48.2
Argon added	
4.41	57.5
4.43	57.5
4.47	57.2
4.52	56.8
4.54	56.2
5.00	56.2

Summary of Above Results.

(1) Sulphur vapour at 100° - 150°C at a pressure of about .01mm. Hg, reacts with oxygen whose pressure is about .3mm. Hg. in the present of a hot filament.

(2) The rate of the reaction is very nearly independent of the oxygen pressure until a pressure of about .1 of a mm. Hg is reached when the re-:action apparently ceases.

(3) The presence of Argon does not appreciably alter the rate of the reaction.

The discussion of these results will be held over until other experiments are described.

Apparatus 11.

This apparatus is the same as 1. except for the reaction vessel. The reaction vessel is a silicatube, 19cm. in length and 4cm. in diameter. Through this tube there runs an axial tube 1cm. in diameter. The volume of the vessel is approximately 50cc. A coil of resistance wire H_1 runs through the inner tube. This coil can be heated electrically to about 500°C, the temperature being read by means of a "Pt.Rd." thermocouple. The main part of the reaction /

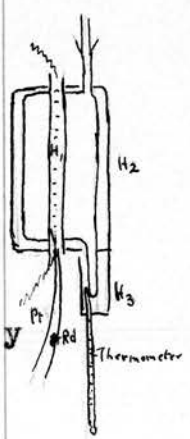


Fig 2.

reaction vessel is in an electric heater H_2 by means of which the outside walls can be maintained at 200°C. The small side tube S contains the solid sulphur and this is heated up to 80° - 100°C by the electric heater H_3. The vessel is connected to the rest of the apparatus by a silica to glass ground joint.

Procedure.

The sulphur was purified as before and then oxygen introduced to the required pressure. The outer walls were maintained at 200°C and the inner tube was heated for a certain time to 400° or 500°C and any change of pressure noted as before. In most of the experiments the sulphur dioxide and trioxide formed was only condensed out by liquid air after the inner tube had been heated i.e. tap T opened after the inner tube had cooled.

Results.

↓ means that centre tube is at 500°C.
↑ means that heater H_1 is switched off.

Sulphur at 84 4C outside walls at 300° ± 10°C
Tap T_6 open throughout experiment.

0

T	R
	Z=46.5
2.59	77.2
3.2	77.3
3.5	77.9
3.20	77.2

1

T	R
	Z=46.5
2.22	74.2
2.30	74.2
2.36	↓
2.36	78
2.37	77
2.39	72
2.40	69
2.41	66.8
2.45	58.5
2.47	55.2
2.50	51.2
2.50	↑
2.55	49

2

T	R
	Z=46.5
3.20	77.2
3.23	↓
3.25	79
3.27	77.2
3.29	74.8
3.30	73
3.31	72
3.33	69
3.38	63.3
3.40	61.5
3.40	↑
3.42	59.2
3.45	57.8
3.50	57.2

Tap T_6 closed while H_1 is at 500°C.

3

T	R
	Z=46.5
3.55	80
3.56	↓
4.14	↑
4.22	59.5
4.24	58
4.26	59

4

T	R
	Z=42.8
12.21	76
12.22	↓
12.43	↑
12.46	76
12.51	57
12.53	56
12.55	56
12.55	↓
1.15	↑
1.20	47.5
1.22	47
1.25	46.8

5

T	R
	Z=43
1.30	90.5
1.30	↓
1.50	↑
1.59	74
2.3	71
2.6	71

Further Results.

Sulphur at 84° + 4° Outside wall at 200° ± 10°

(The sulphur dioxide is condensed out after the heating of H_1)

Oxygen Pressure 1 Div. = .024mm. Hg.	Argon Pressure	Time of heating H_1 at 500°C in minutes.	Change of pressure.
30	-	10	11.5
27	-	10	13
26.3	13.7	10	10
12.8	-	17	10
12.5	-	16	10
13.8	-	13	9
20	-	10	10
9.1	-	10	4.1
10.8	-	10	5
11	-	10	5.7
11	21	10	3.7
12	-	10	5.5
6.5	-	10	4.5
2	-	10	.6
11	20	10	4.7
9.8	16.1	14	5.3
10.1	16.1	10	3.5

The Effect of Changing the Temperature of H_1.

20 Divisions of Oxygen.

Heat 10mm. at 600°	Change of Pressure	15.8 Divs.
500°		11.8 "
400°		10 "

The /

The Effect of Changing the Temperature of S.

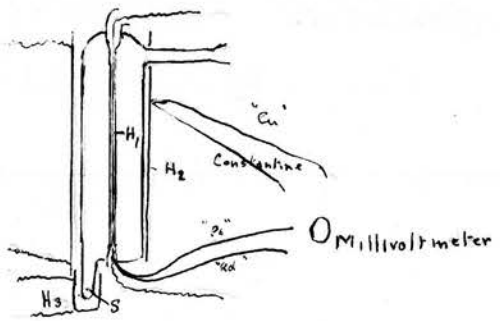
H_1 heated for 10 mins. at 500°.

S at 84° 24 Divisions of Oxygen. Change of Pressure 10.7 Divs.
S at 135° 22.2 " " " " 16.5 Divs.

The above results show (1) The amount of reaction is dependent of time heating. (2) The rate of the reaction is roughly proportional to the pressure of oxygen for pressures below .3 of a millimetre of mercury, when the SO_2 and SO_3 formed is not condensed out during the reaction. (3) The rate of the reaction increased with rise of tempera-:ture of H_1 and also increases as the pressure of the sulphur vapour is raised. (4) Argon has little effect on the rate of the reaction, the tendency of the experimental results is to show a decrease in the reaction rate.

Apparatus 111.

Fig 3



This apparatus is similar to 11. except that a different reaction vessel was used and that a MacLeod /

MacLeod Guage was added. The reaction vessel is of pyrex and is 29cm. in length, 6cm. in diameter. Through the centre runs an axial tube which is 3mm. in external diameter. The pyrex vessel is first wound with sheet copper. Asbestos is placed over the copper and over this is wound resistance ribbon and then more asbestos. The walls of the vessel could thus be heated to 100° to 150° and the temperature found by means of a copper constan-:tine thermocouple. Through the inner tube there runs a length of resistance ribbon which can be heated to 500°C and whose temperature is read by means of a "Pt.Rd." thermocouple.

Preliminary experiments showed that if tap T_6 was closed, the temperature of the outside walls kept at about 127°, and the inner tube heated for a short time to 500°C there was a slow drop in pressure when the tap T_6 was opened.

Apparently it did not matter how long the inner tube was at 500°, for the reaction to go to certain minimum pressure which lay about .05mm. To speed up the rate of condensation of SO_2 and SO_3 tap T_6 was cut out and C was made larger and placed nearer R. When this change had been made, the reaction proceeded at a quicker rate and a luminescence could be seen in the whole volume of the gas. This shows that we are dealing with a chain reaction.

Results. /

Results.

In each case the inner tube is heated until reaction sets in. This takes place in one or two minutes, R.P. signifies the residual pressure as found from MacLeod Guage.

1.
H_2 at 127°
S at 90°

T	R
	Z=47
11.26	60
11.27	57.5
11.28	55
11.29	52.5
11.30	51
11.31	50.5
11.32	50.2
11.33	50
11.35	50
11.35	50

R.P.= .07mm.Hg

2.
H_2 at 127°
S at 83°

T	R
	Z=51
12.44	65
12.45	64
12.46	63
12.47	61.7
12.48	60
12.49	59
12.50	57.8
12.51	56.5
12.52	55
12.52	55
12.54	54
1.40	54

R.P. = .068mm.Hg.

3.
H_2 at 127°
S at 80°

T	R
	Z=51
1.47	65
1.48	64
1.49	63
1.50	62
1.55	55.5
1.56	55
2.1	53
2.10	53

R.P=.068 mm. Hg.

4.
H_2 at 130°
S at 60°

T	R
	Z=51
2.20	65
2.24	62.5
2.27	61
2.30	60
2.33	58.3
2.35	57.5
2.37	56.3
2.45	53
2.55	53

R.P.=.055mm.Hg.

5.
H_2 at 150°
S at 90°

T	R
	Z=50
3.53	57
3.54	55
3.55	53.5
3.57	53
4.00	52.2
4.7	52.2

R.P. = .07mm.Hg.

6.
H_2 at 110°
S at 90°

T	R
	Z=50
4.28	60.3
4.29	59.2
4.30	58
4.31	57
4.33	55.2
4.34	54
4.35	53.2
4.36	52.8
4.38	52.2
4.45	52.2

R.P. = .095mm.Hg.

7.
H_2 at 127°
S at 50°

T	R
	Z=50.5
11	65.2
11.1	64.8
11.2	64.2
11.3	64
11.4	63.8
11.5	63.3
11.6	63.1
11.7	62.9
11.8	62.3
11.9	62
11.10	61.5
11.12	61
11.13	61
11.14	60.2
11.15	60
11.16	59.5
11.17	59.2

T	R
11.18	58.9
11.19	58.3
11.20	58.1
11.21	58
11.22	57.3
11.23	57
11.24	56.8
11.25	56.4
11.27	56
11.28	55.2
11.29	55
11.30	54.3
11.31	53.5
11.32	53.2
11.33	53
11.34	53

7.

T	R
11.34	53
11.36	52.8
11.38	52.5
11.42	52
11.45	52
R.P. = .042mm.Hg.	

8.

H_2 at 150° S at 90°

T	R
	Z=50
5.0	60
5.1	59
5.2	57.5
5.3	56
5.4	54.2
5.5	53
5.6	52
5.7	51.7
5.8	51.2
5.9	51
5.10	51
R.P. = .953mm.Hg.	

9.

H_2 at 127° S at 80°

T	R
	Z=50
12.11	58.5
12.12	57.8
12.13	56.5
12.15	53.3
12.16	54.2
12.17	53.8
12.18	53
12.21	52.9
12.23	52.5
12.25	52.1
12.29	52.1
R.P. = .046mm.Hg.	

10.

H_2 at 105° S at 90°

T	R
	Z=50
2.56	58.8
2.57	57.4
2.58	56.2
2.59	55.2
3.00	54.2
3.1	53.2
3.2	52.7
3.3	52.2
3.4	52
3.6	51.9
3.9	51.1
R.P. = .077mm.Hg.	

11.

H_2 at 155° S at 90°

T	R
	Z=50
2.19	60
2.20	58.5
2.21	57
2.22	55.3
2.23	54
2.24	53.5
2.25	53.2
2.26	53
2.28	52.5
2.30	52
2.34	51.7
2.34	51.7
R.P. = .046mm.Hg.	

12.

H_2 at 105° S at 85°

T	R
	Z=50
3.23	58.5
3.24	57
3.25	55.5
3.27	53.5
3.28	53
3.30	52.2
3.35	52
3.40	52
R.P. = .088mm. Hg.	

13.

H_2 at 95° S at 75°

T	R
	Z=49.8
4.1	63.2
4.2	62.5
4.3	62.2
4.4	62
4.5	62
4.7	61.5
4.10	61
4.12	60.2
4.17	59.5
4.18	59
4.26	58
4.31	57
4.35	56.5
4.40	56
4.45	55
4.50	54.2
4.53	53.9
4.55	53.5
5.0	53
5.5	52.5
R.P. = .11mm.Hg.	

14.

H_2 at 140° S at 92°

T	R
	Z=50.5
11.44	59.1
11.45	58.0
11.46	56.2
11.47	54.2
11.48	53.1
11.49	52.4
11.50	52.2
11.51	52.0
11.52	52.0
11.55	51.8
12.15	51.5
R.P. = .035mm. Hg.	

Effect of Nitrogen.

15.

H_2 at 140°, S at 90° H_1 on throughout

	Z=48.7
3.31	60
3.32	60
3.33	59.5
3.34	58.6
3.36	56.7
3.37	55.6
3.38	54.2
3.39	53
3.40	51.8
3.41	50.3
3.42	50
3.43	49.8
3.44	49.4
3.45	49.2
3.46	49.1
3.47	49
3.50	49
4.0	48.2

R.P. = .035mm. Hg.

16.

H_2 at 127° S at 90°

	Z=49.3
N_2 added to	51.8
O_2 added to	63
1.46	60
1.47	58.8
1.48	57.4
1.49	56.2
1.51	55
1.52	54.5
1.53	54.1
1.55	54
2.00	54

R.P. = .147mm. Hg.
R.P. of O_2 = .09mm. Hg.

17.

H_2 at 127° S at

	Z=48.8
N_2 added to	51
O_2 added to	59
2.57	57.1
2.58	56.5
2.59	56
3.1	54.2
3.2	53.9
3.4	53.2
3.5	53
3.19	53

R.P. = .154mm.Hg.
R.P. of O_2 = .19mm.Hg.

18.

H_2 at 127°
S at 92°

T	R
	Z=45.0
O_2 added	
to	54
after heating	
of H_1 pressure	
falls to	46
On removing	
liquid air from	
C pressure rises	
to	54.
On cooling C with	
CO_2 snow pressure	
falls to	53.2
i.e. about 4%	
SO_3 formed	

19.

H_2 at 140°
S at 86°

T	R
	Z=49.3
3.52	65
3.53	63.5
3.54	62.9
3.55	62.0
3.56	61
3.57	60.2
3.59	58.5
4.0	57.3
4.3	55
4.4	54
4.6	51.9
4.7	51.5
4.9	51
4.11	51

R.P.= .045mm.Hg.

On replacing liquid air by CO_2 snow pressure rises to 64.2 When C is at room temp. pressureis 65.0 i.e. about 7% SO_3 formed.

20.

H_2 at 140°
S at 90°

C is in CO_2 snow instead of liquid air.

T	R
	Z=49
O_2 added	
to	60.5
4.50	61
4.52	60
4.55	60
4.58	59
C is now	
cooled with	
liquid air	
5.1	52

i.e. about 15% SO_3 formed.

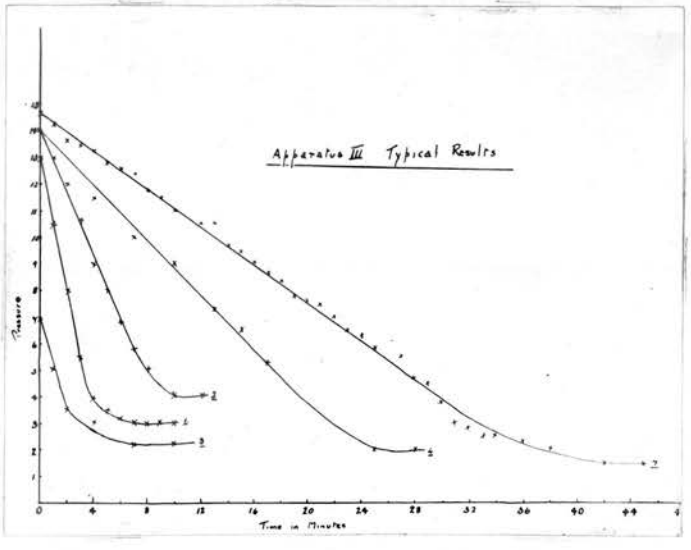


Fig 3A

The above results are shown in graph in Fig. 3A.

Summary of above Results.

1. The reaction goes spontaneously after active centres are formed.

2. The rate of the reaction is practically independent of pressure of oxygen until pressures of about .1mm.Hg. is reached, when reaction stops.

3. The rate of the reaction varies with the temperature of the side tube S, in which is contained the solid sulphur.

4. Even if the temperature of H_1 is kept at 500° throughout we still apparently get a residual pressure i.e. the rate of the reaction (if any) below the lower limit is too small to be measurable.

5. Nitrogen has little effect on the lower limit the experimental result showing a slightly higher value for the residual oxidation pressure.

Apparatus 1V.

A silica flask of about 250cc. capacity was used as the reaction vessel. Sulphur was placed in the flask and the flask kept in water at 100°. About .3mm.Hg. pressure of oxygen was then added and the flask exposed for an hour to a mercury amalgam lamp. No change of pressure was noticed. An iron spark also failed to cause any combination of the sul-:phur vapour and the oxygen.

When a discharge was passed through the vessel /

vessel by means of a Tessla coil, reaction took place as long as the discharge was passing, but did not initiate a reaction which proceeded after the removal of the discharge. If however, oxygen is introduced to a pressure of .6mm.Hg and if a discharge is passed through the vessel for some time, a luminescent reaction is seen after the discharge has stopped.

Discussion.

Let the results obtained in apparatus 111. be first examined. This investigation shows that sulphur vapour at a pressure of about .01mm.Hg and oxygen at a pressure of about .3mm. Hg at a temperature varying from 100° to 150°C can be made to give a luminescent reaction, if the reaction is started by means of a surface at 500°C. This reaction appears to be the same as that obtained by Semenoff and Rjabinin when the reaction is initiated by an electric discharge. The fact that luminescence is present and that the reaction goes spontaneously after the condition which started the reaction has been removed.shows that a chain reaction is present. It has been shown by Alyea, Thompson and others that many "explosions" are initiated on a surface and /

and the above experiment shows that the oxidation of sulphur can also be initiated on a surface. So far it has been impossible to tell whether the reactions are initiated on an absorbed layer on the surface or in the gas phase just off the surface. Work on the effect of wall temperature on chain initiation, as distinct from gas temperature re-:quires to be conducted thoroughly, to obtain a knowledge of the mechanism of chain initiation. In this particular experiment the wall requires to be between 400° and 500° to start the chain. When the middle tube was left at 300° for about half an hour no appreciable reaction was noticed. An inter-:esting point about the reaction is the fact that the rate is independent of the oxygen concentration, and that the reaction shows down as we decrease the temperature of the side tube which contains the sulphur. This appears to show that the rate of the reaction is proportional to some function of the vapour pressure of sulphur. Semenoff and Rjabinin suggest that the rate of the reaction is proportional to the rate of evaporation of the sulphur. A rough calculation can be made to if this assumption is valid. When sulphur vapour is in equilibrium with the solid, the rate of the molecules evaporating from the surface must be equal to the number of molecules striking the surface and hence the rate of evaporation can be calculated as follows.

Rate /

Rate of Evaporation of Sulphur Vapour at 90°C.

Assume that most of the molecules are in the S_8 state; actually only about 90% are S_8. Vapour Pressure = .0025mm. Hg.

Kinetic Energy of Molecule at 0°C = $\frac{1}{2}mu^2 = 5{\cdot}62 \times 10^{-14}$ ergs

" " " 90°C = $\frac{5{\cdot}62 \times 10^{-14} \times 363}{273}$

Velocity of Molecule of S_8 = $\sqrt{\frac{2 \times 5{\cdot}62 \times 10^{-14} \times 363 \times 6{\cdot}06 \times 10^{23}}{273 \times 8 \times 32}}$

$= \underline{1.88 \times 10^4 \text{ cm. per sec.}}$

Number of molecules per cc. at 90°

$= \frac{6.06 \times 10^{23} \times .0025 \times 273}{22.4 \times 1000 \times 363 \times 760} = 6.7 \times 10^{13}$

Number of molecules striking a surface A per sec.

$= \frac{3}{13} \bar{u} n' A$

where n' = number of molecules per cc
$\bar{u}$ = mean velocity

Area of the surface of the sulphur is about .2sq.cm.

Number of molecules striking sulphur per sec.

= Number of molecules leaving the surface per sec.

$= \frac{3}{13} \times 1.88 \times 10^4 \times 6.7 \times 10^{13} \times .2$

$= \underline{5.82 \times 10^{16} \text{ molecules per sec.}}$

i.e. $= \underline{3.49 \times 10^{19} \text{ molecules in 10mins.}}$

If this sulphur was being oxidised at the same rate as it left the surface, the change of pressure in the apparatus, whose volume is about 800cc.

= /

$$= \frac{3.49 \times 10^{19} \times 8 \times 22.4 \times 10^{3} \times 760}{800 \times 6.06 \times 10^{23}}$$

$$= 9.8 \text{ mm. } Hg.$$

As similar calculation for the rate of evaporation at 50° gives a value of .049mm. Hg.

(The vapour pressure at 50° is not accurately known. Recently two students in this laboratory determined the vapour pressure of sulphur at 50° under my supervision. They obtained the value .00015 mm. pressure on the assumption that the sulphur was S_8 and this value has been used in the above calculation)

Change of Pressure.

	If rate was due to rate of evaporation	Found experimentally
50°	.049mm.	.084mm.
90°	9.8mm.	.3mm.

The above calculation appears to show that at 90° the rate of evaporation is much faster than the rate of the reaction while at 50° the rate of evaporation is (within the limit of error) equal to the rate of the reaction. An explanation of this result may be that the rate of the reaction is proportional to the concentration of S_2 molecules or to the rate of formation of S_2 molecules.

The amount of SO_3 formed is found to be very small and is probably formed when the chain propagator is destroyed by colliding with an SO_2 molecule. The fact that nitrogen does not appreciably change the residual pressure appears to show /

show that the reaction chains are not principally broken by the walls. The experimental results of the various experiments appear to show that the chain propagators are destroyed in the gas phase by collision with the product SO_2. In the experiment carried out in apparatus 1. no luminescence was observed, because the SO_2 was not being removed fast enough from the reaction vessel. More chains were being terminated by the propagators being destroyed by collisions with SO_2, than were formed by the propagators colliding with sulphur vapour and oxygen, and hence when the supply of active centres, formed by the hot wall, was cut off the reaction stopped. It would therefore appear that if SO_2 is present the reaction takes place principally at the wall. In the experiments carried out in apparatus 11 the SO_2 formed was not removed and hence the reaction in this case is confined principally to the walls.

Heat of Activation.

A knowledge of the heat of activation of the reaction furnishes some evidence as to the nature of the reaction. The following calculation leads to an estimate of the heat of activation of the reaction obtained in apparatus 11 on the assumption that the hot silica surface contains a layer of sulphur vapour and that reaction takes place when a molecule /

molecule of O_2 strikes this surface.

Volume of the apparatus = 50cc. Temperature of gas about 280°.

When the pressure of oxygen is .5mm.

Number of molecules of oxygen present.

$$= \frac{.5 \times 50 \times 273 \times 6.06 \times 10^{23}}{22.4 \times 10^3 \times 550 \times 760} = \underline{\underline{4.4 \times 10^{17} \text{ molecules}}}$$

Velocity of a molecules of oxygen.

$$= \bar{u} = \sqrt{\frac{2 \times 5.62 \times 550 \times 10^{-14} \times 6.06 \times 10^{23}}{273 \times 32}}$$

$$= \underline{\underline{6.55 \times 10^4 \text{ cm per sec}}}$$

Number of molecules hitting the 500°c surface per sec.

$= \frac{3}{13} \bar{u} n' A$ (n', number of molecules in a cc. A =area of surface)

$$= \frac{3}{13} \times 6.55 \times 10^4 \times 9 \times 10^{15} \times 30$$

$$= \underline{4.08 \times 10^{21} \text{ per sec.}} = \underline{2.45 \times 10^{24} \text{ in 10 mins.}}$$

Now the change of pressure in 10 mins. found experimentally =.24mm. = $\underline{2.2 \times 10^{17}}$ molecules O_2 have reacted.

Number of molecules that react on striking surface / Number of molecules that strike the surface

$$= \frac{2.2 \times 10^{17}}{2.45 \times 10^{24}} = \underline{\underline{9 \times 10^{-8}}}$$

Therefore nearly 1 out of 10^7 collisions are effective in giving reaction.

$$2.303 \log_{10} \text{Prob of Reaction} = -\frac{E}{RT}$$

$$\therefore \quad 7 = \frac{E}{1.98 \times 800 \times 2.303}$$

$$E = 7 \times 1.98 \times 800 \times 2.303$$

$$= \underline{26{,}000 \text{ calories approx.}}$$

This value is in quite good agreement with the apparent heat of activation found by Norrish and Rideal.

The above investigation makes it apparent that what may appear to be a pure surface reaction can easily be a chain reaction where the length of the chain is confined to a few links, because of the deactivation of the chain propagator by the product. This hypothesis may explain some of the difficulties in connection with the apparent heat of activation of surface reactions. The above results also raise the interesting problem of the mechanism and of the conditions necessary to change a surface reaction into a chain reaction initiated by the surface.

Part 111.

The Influence of Foreign Gases on the Lower Critical Oxidation Pressure of Carbon Disulphide.

(This is the text of a paper submitted to the Royal Society of London under the names of Ritchie, Brown, and Muir. Brown and Muir are two B.Sc. students who assisted me with some of the experi-:mental work)

The study of gaseous reactions has recently acquired additional interest since it has been found that a considerable number of reactions can be explained on the basis of a chain hypothesis. In 1923 Christiansen and Kramers[1] studied the kinetics of a unimolecular reaction and found that explosion is possible if the total change of energy resulting from the reaction is greater than the energy of activation. Since that time the mechanism of chain reactions has been carefully investigated and some of the conditions for the continued propagation of the reaction have been ascertained.

Thus if we have two gases mixed together without any chemical change taking place, a reaction may commence when even a very small quantity of a third molecule is added, or if one of the original molecules receives energy of activation (from whatever cause). Designating the original molecules for simplicity by A and B and the new molecule by C, which we will suppose reacts with A giving a fourth molecule D (and possibly other molecules also), we have

$$A + C \longrightarrow D$$

If then D reacts with B producing more C (as well as other products)

$$B + D \longrightarrow C + \text{etc.}$$

C and D are continually produced and form links in a chain, enabling the reaction to proceed. If the amount of C and of D formed in unit time is

greater than the amount destroyed, the chain will have many branches, i.e. the reaction auto-accelerates and explosion occurs. The active centres C and D may be destroyed in two ways (a) by collision in the gas phase (b) by collision with the surface of the vessel. These considerations show that the amount of C and D formed and destroyed in unit time varies with the concentration of the gases A and B. There may be a definite range of concentration in which the rate of formation of the active centres exceeds the rate at which they are destroyed, i.e. in which "explosion" can occur. Many reactions are satisfactorily explained by this hypothesis. Phosphorus vapour and oxygen, sulphur vapour and oxygen, hydrogen and oxygen, carbon disulphide and oxygen, are found to unite explosively only between certain limits of pressure and Semenoff[11],[7] showed that this is explicable by means of the theory of chains. He investigated the effect of the presence of foreign gas and the effect of varying the diameter of the reaction vessel on the lower oxidation limit and obtained the following relation

$$p_{P_4}^{\frac{1}{2}}\, p_{O_2}\left(1+\frac{p_x}{p_{P_4}+p_{O_2}}\right) d^2 = K$$

p_{P_4} is the pressure of phosphorus vapour. p_x the pressure of foreign gas, p_{O_2} is the critical oxidation pressure, d the diameter of the reaction

vessel /

vessel and K a constant over a considerable temperature range. Dalton and Hinshelwood[14] found that this equation also held when phosphine was substituted for phosphorus vapour.

The equation can be derived theoretically by the assumption that below the critical pressure the chains are being broken so efficiently by the walls, that the concentration of active centres remains stationary. The foreign gas molecules impede the chains reaching the wall and so lower the critical oxidation pressure. The equation should hold for all similar chain reactions, but it must be noted that it is only approximately true. Melville and Ludlam[15] investigated the effect of a large number of gases and organic vapours on the oxidation of phosphorus and although they found that straight lines were obtained when $\frac{1}{p_{O_2}}$ was plotted against $1 + p_x/p_{P_4}+p_{O_2}$ (p_{P_4} being kept constant), these lines had not the same slope $\frac{d^2}{K}$ as is expected from the above equation. Melville and Ludlam showed that the differences were in the main due to the different rates of diffusion of the chain propagators into the foreign gases. Melville[9] has recently given a theoretical equation for this foreign gas effect. He finds that p_X should be multiplied by a factor inversely proportional to the diffusion coefficient of the chain propagators into the gases present.

The factor is, $f D_x^{-1} = \sigma_{Ax}^2 \left(\frac{1}{M_A} + \frac{1}{M_x}\right)^{-\frac{1}{2}} / k$

where M_A and M_X are the molecular weights of the diffusing molecules A and of the foreign gas X respectively. σ_{Ax} is the sum of the radii of A and X. M_A and σ_A will be mean values as they represent the effect of two chain propagators. Thompson[20] has recently found that the foreign gases change the lower critical explosion pressure of hydrogen oxygen mixtures in the same order as was found by Melville and Ludlam. In this case active centres were introduced by an electric spark.

The critical pressure limits of the carbon disulphide oxygen explosion have been investigated by Thompson[22]. His researches show that the active centres of the chain are principally formed at a hot wall.

In the present investigation the carbon disulphide and oxygen were kept at room temperatures and the hot wall furnished by a glass covered tungsten filament, and an ordinary tungsten filament. It was found that this method gave the pressure of foreign gas at the lower critical oxidation pressure to within 1 mm. of mercury. The object of the present work was to investigate the effect of several gases and organic vapours on the lower critical oxidation pressure for $CS_2:3O_2$ mixtures with a view to testing the applicability of Semenoff's equation with Melville and Ludlam's correction.

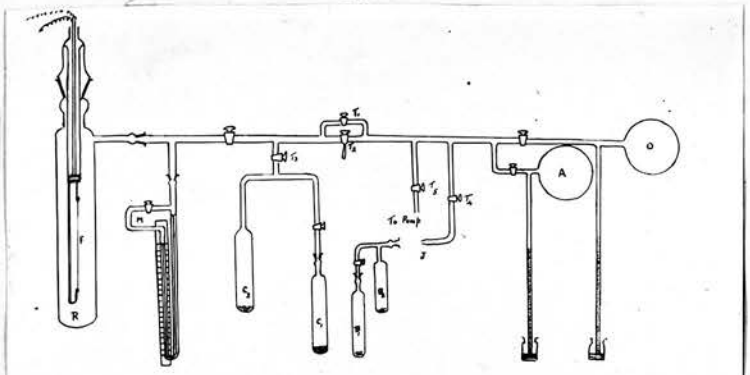


Fig. 1. Diagram of the reaction tube R showing connections to oxygen reservoir O, to the foreign gas reservoir A, and to the CS_2 reservoir C_2.

APPARATUS AND PROCEDURE.

The apparatus is shown diagramatically in Fig. 1. R is the reaction tube which is 25cm. in length and 2·5cm. in diameter. The filament F is mounted on a degassed nickel support, which is attached to borated copper wire, which in turn passes to the outside of the vessel through a pinch seal. The whole arrangement is mounted on the ground glass joint of the reaction tube. The glass filament is prepared as follows. Pyrex tubing is drawn down to a fine capillary which is threaded with 0·1 mm. tungsten wire and the glass melted on to the wire electrically in vacuo. Glass ends are now fitted on and filled with lead into which pass copper wires. This type of filament was first used by Melville in connection with the stable chain oxidation of Phosphorus. Actually most of our experiments were conducted using a plain tungsten filament. This was only heated to a dull redness and so practically no oxidation took place. The results /

The results show that there is little difference in the behaviour of the two filaments. M is a sulphuric acid manometer with scale attached. C_1 contains the carbon disulphide, A and O are reservoirs for foreign gas and oxygen respectively. When organic liquids are used they are placed in B_1, which is then connected to the rest of the apparatus at J.

The procedure is as follows. The apparatus is evacuated using an electrically driven oil-pump, C_1 being immersed in liquid air. Tap T_3 is closed and some carbon disulphide distilled into C_2. The taps T_1 and T_3 are now closed and A and O filled with the foreign gas and oxygen to a pressure of about 20mm. of mercury through tap T_4. Carbon disulphide vapour is now introduced into the reaction vessel to the desired pressure as read from the manometer. Oxygen is then admitted to about three times that pressure. The filament is switched on for one or two seconds. If the pressure is below the critical value no flash is seen and the manometer reading remains the same. The foreign gas is now admitted in small quantities by means of the tap-pipette T_2 and the filament heated after each addition. At a certain pressure of foreign gas an explosion takes place and the pressure falls. The explosion is accompanied by a blue luminescence.

Organic liquids were distilled in vacuo

from /

from B_1 to B_2 and their vapours admitted by the tap-pipette into the reaction vessel. In the case of hydrogen the oxygen had to be introduced afterwards for reasons which will appear later. The oxygen, nitrogen, argon, hydrogen and carbon dioxide were all obtained from cylinders and were dried by passing them over phosphorus pentoxide. Sulphur dioxide was obtained from a syphon of the liquid. The carbon disulphide was previously distilled and the middle fraction used. The carbon tetrachloride was sulphur free. The table below shows some of the experimental results. All pressures are in millimetres of mercury.

Inert Gas X	p_{CS_2}	p_{O_2}	p_X (inert gas)	$\frac{1}{p_{CS_2} p_{O_2}}$	$1 + \frac{p_X}{p_{CS_2} + p_{O_2}}$
	3.7	16.9	0	.0162	1.00
Carbon	3.9	12.6	4.9	.0205	1.30
Dioxide	3.8	11.4	6.9	.0231	1.45
	3.4	10.2	11.0	.0288	1.81
	2.7	8.1	23.8	.0457	3.20
	3.7	16.8	0	.0163	1.00
Sulphur	4.1	12.9	3.7	.0192	1.22
Dioxide	3.5	11.2	9.6	.0253	1.65
	3.2	10.3	12.6	.030	1.93
	3.0	9.3	16.8	.0359	2.36
	4.0	15.7	0	.0159	1.00
	4.0	12.4	19.1	.0204	1.62
Nitrogen	3.7	15.1	4.3	.0181	1.23
	3.5	10.8	21.9	.0263	2.53
	3.0	9.3	35.2	.0359	3.86
	3.6	16.6	0	.0169	1.00
Argon	4.2	12.6	4.2	.0189	1.25
	3.8	11.8	9.9	.0224	1.63
	3.2	9.7	19.1	.0317	2.47
Argon using	3.4	10.3	8.2	.0287	1.6
a glass -	2.7	8.1	12.8	.0456	2.18
covered filament	2.3	7.3	16.1	.0596	2.68

Inert Gas X	p_{cs_2}	p_{o_2}	p_x (inert gas)	$\frac{1}{p_{cs_2} p_{o_2}}$	$1 + \frac{p_x}{p_{cs_2} + p_{o_2}}$
	3.9	16.4	0	.0156	1.00
	3.8	20.3	13.8	.0130	1.57
	3.7	27.4	27.0	.0100	1.87
Hydrogen	3.5	31.4	38.2	.0090	2.09
	4.0	18.1	11.3	.0138	1.51
	3.9	24.1	5.0	.0106	1.18
	3.7	26.5	12.3	.0104	1.41

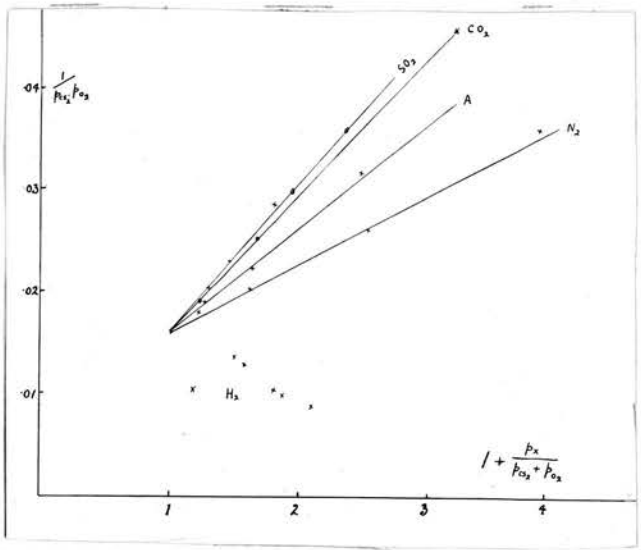


Fig 2

DISCUSSION.

As shown in Fig. 2 when $\frac{1}{p_{cs_2} p_{o_2}}$ is plotted against $\left(1 + \frac{p_x}{p_{cs_2} + p_{o_2}}\right)$ satisfactory lines are obtained except in the case of hydrogen. The slopes of the lines given by argon, nitrogen, carbon dioxide and sulphur dioxide follow the same order as was found by Melville and Ludlam for the $P_4 : O_2$ explosion. Assuming $p_{cs_2} p_{o_2} \left(1 + \frac{f D_x^{-1} p_x}{p_{cs_2} + p_{o_2}}\right)$ = constant (= $p_{cs_2} p_{o_2}$ when no foreign gas is present) the above experimental results give the following values for $f D_x^{-1}$

Foreign Gas	Nitrogen	Argon	Carbon Dioxide	Sulphur Dioxide.
$f D_x^{-1}$	.42	.64	.83	.92

These values are not sufficiently accurate to enable a calculation of the molecular weight of the chain propagator to be made using the expression $\frac{\sigma_{Ax}^2 \left(\frac{1}{M_A} + \frac{1}{M_x}\right)^{-\frac{1}{2}}}{R}$ for $f D_x^{-1}$

Hydrogen gives an abnormal result, the presence of hydrogen instead of reducing the value $p_{cs_2} p_{o_2}$ actually increases it. This result is accounted for in the following way. In all the other experiments, the change of pressure after exploding was always about 80 to 90% of the original pressure of carbon disulphide. This means that the main reaction gives sulphur dioxide and carbon dioxide.

When /

When hydrogen was present the change of pressure after explosion was approximately one and half times the pressure of the hydrogen. The main reaction is therefore the formation of water from hydrogen and oxygen. It therefore appears probable that we were dealing with the $H_2:O_2$ explosion and that CS_2 was behaving as an inert gas by preventing the $H_2:O_2$ ch in propagators reaching the wall.

TABLE II.

p_{H_2}	p_{O_2}	p_{CS_2}	$\frac{1}{p_{H_2} p_{O_2}} \times 10^2$	$1 + \frac{p_{CS_2}}{p_{H_2} + p_{O_2}}$
13.8	26.3	3.8	.357	1.11
27.0	27.4	3.7	.137	1.07
38.2	31.4	3.5	.083	1.05
11.3	18.1	4.0	.489	1.14
5	24.1	3.9	.830	1.13
12.3	25.5	3.7	.307	1.09

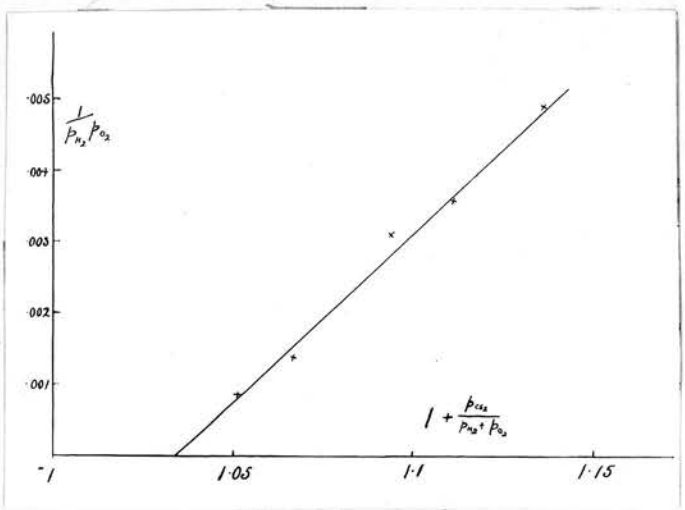


Fig. 3

When $\frac{1}{p_{H_2} p_{O_2}}$ is plotted against $1 + \frac{p_{CS_2}}{p_{H_2} + p_{O_2}}$ as shown in Fig. 3 a straight line is obtained, if the value obtained for a very small pressure of hydrogen is excluded. A peculiar fact about this line is that it appears to show that the $H_2:O_2$ explosion is impossible, under the experimental conditions unless carbon disulphide is present. It is therefore very probable that CS_2 acts as an explosion sensitisor for the $H_2:O_2$ reaction. The propagator of the $CS_2:O_2$ explosion chain may give on colliding with H_2 an active centre, which can start the propagation of the $H_2:O_2$ chain. Carbon disulphide therefore can be looked upon as a catalyst of the reaction under the special conditions of these experiments.

The effect of carbon tetrachloride and of benzene on the lower critical pressure was complicated as neither of these capours acted as "inert" gases. When a certain pressure of benzene or of carbon tetrachloride was reached, on heating the filament a cloud of white particles was formed and a deposit was left on the walls. This pressure was just about where explosion would be expected if these vapours behaved as inert gases. It is probable that the active centres are decomposed on colliding with the organic molecules to give sulphur or complicated compounds.

Thompson /

Thompson found that it was difficult to get reproducible results for the explosion limit owing to variations of the surface of the reaction vessel. There was no difficulty of this kind in the above experiments, as after one or two explosions, which yielded high values, steady results were obtained. The explosion gave no apparent deposit on the walls, but it is very probable that the surface is covered with a thin layer of sulphur or a compound of sulphur, so that further explosions do not change the nature of the surface. The fact that the explosion limit changes with the surface is evidence that chains can be reflected from a surface as well as broked by that surface.

Below the lower critical limit a blue luminescence could be seen round the hot filament, but no change of pressure was observed. This luminescence is taken as evidence of a <u>stable</u> chain reaction below the critical limit similar to the $P_4:O_2$ stable chain found by Melvile and Ludlam[28]. The luminescence observed by Thompson during the induction period is probably due to this type of stable chain. Further examination of the luminescence below the lower limit will shortly be carried out.

In conclusion we wish to thank Dr. Ludlam and Mr Melville for their interest and advice while the work was in progress and the Moray Fund for a grant to /

to one of us (A.R.) towards the cost of apparatus.

SUMMARY.

The lower critical oxidation pressure of carbon disulphide vapour in presence of "inert" gases has been found to obey the expression

$$p_{cs_2}\, p_{o_2}\left(1 + \frac{f D_x^{-1} p_x}{p_{cs_2} + p_{o_2}}\right) = \text{constant}$$

where p_{cs_2} and p_{o_2} are the lower critical explosion pressures in the presence of pressure p_x of inert gas. D_x is the diffusion coefficient of the chain progagator into the foreign gas.

The effects of hydrogen, carbon tetrachloride and benzene, which do not behave as "inert" gases are discussed.

Part 1V.

Preliminary Experiments.

The Reaction of Hydrogen Sulphide on the Halogens.

Preliminary Experiments.

Introduction:

The type of chemical reaction which has always excited great interest in Chemistry is that which is accompanied by a flame i.e. of radiations from the infra-red to the visible. Nevertheless in spite of the interest and importance of flames in ordinary life it is only within the last few years that experimental investigation has led to a know-:ledge of some of the most important processes occurring in the flame. Flames have been studied from different points of view by different investi-gators. To give a complete description of the various recent investigations, all of which are worthy of close examination, would take too long for the present purpose and I will therefore confine myself to giving a general idea of the type of experiment and of the results accruing from it.

Garner (29) and co-workers have investigated the conditions necessary for the existence of a flame and the effect of foreign gases on these conditions. They have also studied the infra-red radiations from the flame under varying conditions. These experi-:ments enable one to discover the reactions which take place in the flame under different conditions. Garner was also the first to suggest that chain reactions started from a surface.

Henri, /

Henri, Kondratjew, Ludlam[1][30] and others have investigated the visible and ultra-voilet spectra of flames and have thereby obtained a knowledge of the molecules which give certain flames their colour, and also a knowledge of the various excited states of these molecules.

Polanyi[31] and co-workers have confined their attention to highly dilute ('Hochverdünnte') flames. The highly dilute flames studied were the action of sodium vapour on chlorine and on organic halides. By an examination of the distribution of the deposit of the "flame" on the one hand and of the diameter of the "flame" on the other it has been found possible to calculate the activation heat of the reaction. The evaluation of the activation heat is of assistance in putting the organic reactivity work on a sound theoretical footing.

In view of the above experiments which have led to results of theoretical importance a number of preliminary experiments on sulphur flames were investigated to see if suitable flames could be obtained for detailed work of the above kind.

Experimental.

Reaction of Hydrogen Sulphide on Chlorine.

The reaction of hydrogen sulphide on chlorine was first tried to see if this would give a suitable flame. Hydrogen sulphide and chlorine react on mixing to give a deposit of sulphur if hydrogen sulphide /

sulphide is in excess. Under ordinary conditions of temperature and pressure this reaction is accompanied by no luminescence. In the following experiments the hydrogen sulphide was obtained from a Kipp by the usual method and the chlorine was obtained from a cylinder. When hydrogen sulphide was burnt at a nozzle in air and then plunged into a jar of chlorine, the hydrogen sulphide continued burning in the chlorine. The colour of the flame changes from blue to a greenish blue. Since chlorine was in excess when the experiment was conducted in this way no sulphur was deposited, but sulphur chlorides were formed. It was found that hydrogen sulphide could be induced to burn in chlorine by using " $Mn O_2$ ", " $Pb O_2$ ", other similar oxides and charcoal. The presence of a small quantity of these substances started the flame, which then continued unaided. Using the same contact agents, chlorine could be induced to burn at a nozzle in hydrogen sulphide. If the flame was extinguished by placing the nozzle against the side of the vessel, ignition very often took place again when the nozzle was placed in the centre of the vessel. When the hydrogen sulphide: oxygen flame was blown out and the nozzle immediately plunged into chlorine the hydrogen sulphide very often ignited in the chlorine. This might mean that the H_2S: Cl_2 flame requires a lower temperature for ignition than the H_2S:O_2 flame, or that a hot silica nozzle acts as a contact agent.

Experiments /

Experiments were conducted to see if the flame could be initiated by means of light. For this purpose the chlorine was placed in a silica flask, which was exposed to the light of carbon, zinc or iron arcs, and hydrogen sulphide passed into the flask from a nozzle. The light did not induce inflammation. The opposite experiment of passing chlorine into hydrogen sulphide gave no indication of luminosity. Attempts were made to obtain a photograph of the spectrum of the $H_2S:Cl_2$ flame using the simple apparatus shown in Fig.1, at atmospheric and at lower pressures. The flame was lit from the top by a jet of hydrogen sulphide burning in air. The speed of the flow of hydrogen sulphide relative to that of the chlorine depended upon whether it was wished to have the chlorine or the hydrogen sulphide burning at the nozzle. The pressure was reduced by placing a one-holed stopper at the top of the tube and connecting this to a water suction pump. Owing to the difficulty of maintaining a steady flame for a long period and because of the unpleasant nature of the gases the experiments were not prolonged. The only spectrum photographed was indistinct and was obtained with an exposure of half an hour of the flame of hydrogen sulphide burning in chlorine at a pressure of half an atmosphere. This spectrum showed the well known S_2 bands, but was not good enough to identify any SCl bands if they are present.

The /

The reaction between hydrogen sulphide and chlorine may go in two stages:

(1) $H_2S + X\ Cl_2 = 2\ H\ Cl + (S) + (x-1)\ Cl_2$

(2) $(S) + (x-1)\ Cl_2 = (S)\ Cl_y + Z\ Cl_2$

Because of this possibility it was thought to be of interest to investigate the reaction between sulphur and chlorine. Chlorine gas reacts readily with solid sulphur even at low temperatures, but an attempt was made to see if it was not possible to make sulphur "burn" in chlorine or chlorine "burn" in sulphur vapour. For this purpose the silica tube shown in fig.2 was used. The pressure of chlorine was maintained at about 20 mm. by means of a water suction pump. When the sulphur was heated to a suitable temperature ignition took place at the surface of the sulphur, the flame being bluish green. Owing to the difficulty of maintaining this flame no attempts were made to obtain a spectum photograph of it.

Experiments were then conducted to see whether quantitative information could be obtained about the ordinary gaseous reaction, which takes place when hydrogen sulphide and chlorine are mixed. This is very difficult as the reaction is accompanied by no change of pressure.

$2H_2S + 2Cl_2 = 4HCl + S_2$ (H_2S in excess)

If /

If chlorine is in excess we have the complication of the various sulphur chlorides which may be formed. As far as could be seen from simple experiments, hydrogen sulphide reacts instantaneously with chlorine at pressures between 30mm.Hg and 1 atmosphere. These experiments were carried out by having two bulbs connected by means of a tap. One of the bulbs was filled with a certain pressure of dry hydrogen sulphide and the other filled with a higher pressure of chlorine. When the tap was opened a deposit of sulphur was immediately formed.

Reaction of Hydrogen Sulphide on Iodine.

Preliminary experiments on the reaction of hydrogen sulphide and iodine were then carried out. A silica flask was fitted with a three-holed stopper, by means of which glass tubes were connected to a suction pump, to a hydrogen sulphide apparatus and to a mercury manometer, the surface of the mercury being covered with a layer of paraffin oil. Solid iodine was placed in the flask and the pressure of iodine vapour was varied by keeping the vessel in hot water at different temperatures. Hydrogen sulphide was introduced into the vessel and any change of pressure noted. There was no apparent deposit of sulphur and no change

of /

of pressure was noticed. If a reaction took place the pressure would increase as the vapour pressure of iodine remains constant and one volume of hydrogen sulphide would give rise to two volumes of hydrogen iodide. The light of a mercury vapour lamp apparently did not cause any reaction to take place, as the slight increase of pressure which was observed when the vessel was illuminated by the lamp disappeared when the source of light was removed. This change of pressure was probably a "Budde" effect.

As reactions in <u>solutions</u> of non-associated solvents frequently resemble closely reactions in the gaseous state, experiments were conducted on the reaction of iodine and hydrogen sulphide in a solution of hexane and of carbon tetrachloride. The first experiments were carried out in hexane solution and the amount of reaction in a given time was determined colorometrically. The commercial hexane was purified by mixing with sulphuric acid, by separating, by washing with water and by drying with calcium chloride and phosphorous pentoxide.

20 cc. of an iodine solution were placed in four Nessler tubes then in Nessler tubes

(1) and (2) were placed 20cc. pure hexane a d in Nessler tubes (3) and (4) were placed 20 cc. of hexane saturated with hydrogen sulphide.

(1) /

(1) and (3) were exposed to the light of a 200 watt lamp and (2) and (4) were kept in the dark for two hours. Then to match the colours of (2) and (4) 10.5cc. of solution required to be removed from (2). To match the colours of (1) and (3) 23.5cc. of solution required to be removed from (1).
To match the colours of (2) and (1) 3cc. of solution required to be removed from (2).
This experiment appeared to show that the light accelerated a slow reaction which takes place in the dark.

Effect of Moisture.

A further experiment showed that the above reaction was due to a trace of moisture. A solution of iodine in carbon tetrachloride was mixed with one of hydrogen sulphide in carbon tetrachloride and kept in a stoppered bottle for three days in (the dark?) the presence of phosphorus pentoxide without any reaction taking place.

Reaction of Hydrogen Sulphide on Bromine.

Since the H_2S:Cl_2 reaction goes very fast, and the H_2S:I_2 reaction not at all in the dry state, it was thought that the H_2S:Br_2 reaction would go at a measurable rate so that an estimation of the heat of activation could be obtained. The experi-:ment was first of all conducted in carbon tetrach-:loride solution in stoppered bottles and the amount of the reaction was determined colorometri-:cally. Bottles 1,2,3 and 4 contained 20cc. of a solution /

solution containing 1, ½, ¼ and ⅛ parts of bromine respectively. In bottle 5. there was placed 10cc. of carbon tetrachloride solution containing 1 part of bromine (twice the strength of the solution in 1.) and to this was added 10cc. of carbon tetrachloride saturated with hydrogen sulphide. The rate of the reaction was determined by matching the colour of bottle 5 with one of the standards at various times after mixing. If the experiment was carried out with dry solutions in bottles which are dry in the ordinary sense the reaction apparently goes to completion immediately on mixing. Experiments were then carried out in presence of phosphorus pentoxide in bottles which had been stoppered up for several hours with this drying agent. When the reaction was carried out in this way its speed was greatly reduced. The results obtained varied from experiment to experi-:ment but were of the order of

½ Bromine reacting in 2 minutes.

¼ " " " 5 "

It was difficult to know whether the variation of the rate of the reaction was due to the degree of dryness or to the variation of the phosphorus pentoxide surface. To see whether the reaction would go at all if the solutions were absolutely dry the apparatus shown in Fig. 3 was used. The inner /

inner tube (a) had at its end a very thin glass bulb, and in this tube there was sealed a solution of bromine in carbon tetrachloride, and phosphorus pentoxide. In the outer tube (b) was sealed the small tube (a) and a solution of hydrogen sulphide in carbon tetrachloride, and phosphorus pentoxide. The tubes were then left for a day so that any moisture was taken up by the phosphorus pentoxide. The inner tube was then broken by shaking and the solutions mixed. In spite of this efficient method of drying, the colour of the bromine had disappear-:ed in about an hour showing that a reaction had taken place. Another apparatus, which is shown in Fig. 4 was then used in an attempt to obtain quantitative results with really dry solutions. The vessels A and B which contain respectively hydrogen sulphide and iodine solutions with phos-phorus pentoxide, were placed in liquid air and the apparatus evacuated my means of an oil pump. The tubes A and B were left in liquid air for a fairly long time to remove any moisture from the rest of the apparatus to A and B. The liquid air was then removed and the apparatus left for two hours so that the phosphorus pentoxide could pick up any moisture. The solutions were then distilled over into X and Y by means of liquid air, and then the solutions run into C. This method allows the dry solutions to mix in absence of phosphorus pentoxide.

After /

After about two hours about half of the bromine had reacted and after leaving overnight nearly all the bromine had disappeared. These experiments were not continued as it was thought that the reaction might only be taking place because of traces of moisture on the surface of the vessel.

The reaction of hydrogen sulphide and bromine in the gas phase was now investigated using the apparatus shown in Fig. 5. The reaction vessel was divided into two partitions by a thin glass bulb which could be broken by a glass hammer (ie.a glass tube with a knife edge filled with iron filings). Vessel C contained bromine and phosphorus pentoxide. Hydrogen sulphide was first passed through trap D and then was collected in trap D by means of liquid air. To ensure that the hydrogen sulphide was free from dissolved air A was evacuated, then tap T, was opened and the trap D allowed to warm up, Some hydrogen sulphide was thus allowed to escape, through the mercury in E. Tap T, was then closed and the hydrogen sulphide frozen up again. The vessel C was then placed in liquid air and A and B were evacuated by a "hyvac" oil pump. During the evacuation A and B were heated with a bunsen to dry off the walls. After evacuating A and B thoroughly the apparatus was sealed up at the constrictions 2, by means of a blow pipe. The part A of the vessel was then filled to a

pressure /

pressure of 80mm. Hg. (with hydrogen sulphide), and the apparatus sealed off at the constriction Y. Bromine was now introduced into B to a pressure of 65mm. by placing vessel C in ice water, and the apparatus sealed off at X. The glass partition was now broken by means of the glass hammer. The gases mixed together very slowly, but the rate of the reaction appeared to be much slower than the rate of mixing. After three or four hours the reaction had gone to completion. In spite of the precautions taken against the presence of moisture it can not be definitely stated that moisture was absent. Since the slightest trace of moisture might start the reaction, it is therefore not certain whether the reaction would go at all if moisture was entirely absent (i.e. dryness in the "Bakerian" sense). The results can be summarised as follows.

Under ordinary conditions of dryness bromine reacts with hydrogen sulphide fairly slowly, but whether this reaction is a gaseous or a surface reaction could not be determined.

Experiments with Sulphur Monochloride.

The experiments on the H_2S: Cl_2 reaction brought to our notice the sulphur chlorides. As apparently the absorption spectra of gaseous sulphur monochloride (S_2Cl_2) had not been studied a few experiments of this /

this kind were carried out. The commercial sulphur monochloride was purified by mixing with carbon and distilling under reduced pressure. As a source of continuous light a tungsten filament lamp with a silica window was used. As can be seen from plate 1 no interesting discrete absorption bands were obtained. The absorption is very great at wave lengths smaller than 3650 Å . The absorption spectra of the solution of S_2Cl_2 in carbon tetrachloride is very similar.

An attempt was made to get a "Raman Spectrum" of"S_2Cl_2" liquid, but this was abortive.

The emission spectrum of "S_2Cl_2" was taken using the apparatus shown in Fig. 6. The discharge through the vessel was obtained using an induction coil and external electrodes. The spectrum obtained is shown in plates 2+3. Later experiments showed that these bands were similar to those obtained in the emission spectrum of carbon disulphide and are probably due to traces of organic impurity.

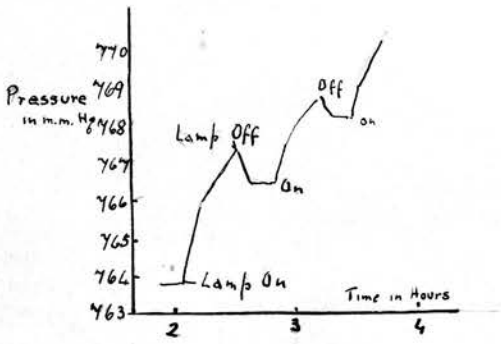
Since the continuous absorption of S_2Cl_2 is probably due to decomposition of S_2Cl_2 into S_2Cl + Cl or S_2 + Cl_2, it was thought that S_2Cl_2 should give a photochemical reaction with hydrogen. These experiments were not entirely satisfactory and therefore will /

will not be described at any length. The two pieces of apparatus used are shown in Figs. 7 and 8.

Apparatus 7 consists of a quartz vessel A which is connected to a glass spring guage G by means of a silica to glass graded tube. The pressure in the apparatus was read by bringing the pint of the guage back to "zero" by means of a water mano-:meter. The reaction vessel with the gauge was placed in a thermostat with a silica window. After evacuation sulphur monochloride was distilled into B. The apparatus was then filled with about one atmosphere of hydrogen which was purified by passing over palladium abbestos in the usual way as shown in the sketch. When the vessel was illuminated by a mercury vapour lamp the pressure was observed to rise. During the experiment however the side of the vessel through which the light entered became covered with liquid sulphur chlorde. The reason for this accumulation of sulphur chloride is because sulphur is deposited on the surface of the vessel by the action of light, and this sulphur forms a nucleus for the condensation of sulphur monochloride.

The vessel shown in Fig 8 was entirely of silica and this was connected by means of a silica to glass ground joint to the hydrogen source at Y, shown in Fig.7. The "S_2Cl_2" liquid itself served as a mano-meter. The level of the right limb was read by means of a sliding microscope and the pressure then calculated. /

To enable the apparatus being evacuated, the sulphur monochloride was frozen by means of liquid air. The apparatus was then evacuated by the "hyvac" pump and filled with hydrogen to approximately atmospheric pressure. The apparatus was then placed in a trans-:parent vacumn flask filled with ice and water, and the cell A exposed to the light of a mercury vapour lamp. When the pressure was plotted against time the following type of curve was obtained.



If the apparatus was allowed to stand for one or two days after filling it with hydrogen, the light had no effect. The reason of this might be that the reaction was due to traces of moisture and that this moisture was gradually attacked by the sulphur monochloride on standing. The experiments were dis-:appointing in that the numerical results obtained were not reproducible.

In order to see if any bands such as "SCl" were present, air was burnt in hydrogen containing "S_2Cl_2" vapour and a spectrum photograph of the flame taken. The bands obtained were identical with those obtained when /

when air is burnt in hydrogen which contains a trace of "H_2S", and is due to "S_2" and "SO" (Plate 4)

It was noticed that when alcohol containing a small amount of chloroform was burnt in a spirit lamp a brilliant blue was obtained. As the apparatus was available and because it was thought that some interesting bands such as "C Cl" might be found a spectrum photograph of this flame was obtained. The bands were measured with the result shown in the table. They were identified as being due to "Cu Cl", the source of the copper being the brass ring of the wick holder.

Plate 5

λ measured	λ for CuCl (from Kayser's Handbuch)
4576	4579
4522	4515
4494	4494
4432	4433
4417	4412
4354	4354
4325	4333

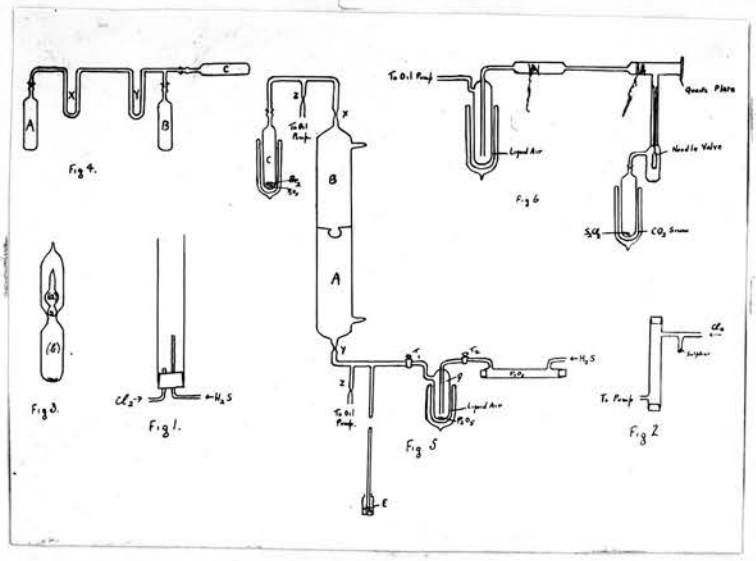
In conclusion I heartily thank Dr. E.B. Ludlam under whose supervision the research was carried out, for advice and encouragement and also Professor Kendall for his continued interest. My thanks are also due to the Trustees of the Earl of Moray Fund for a grant towards the cost of apparatus.

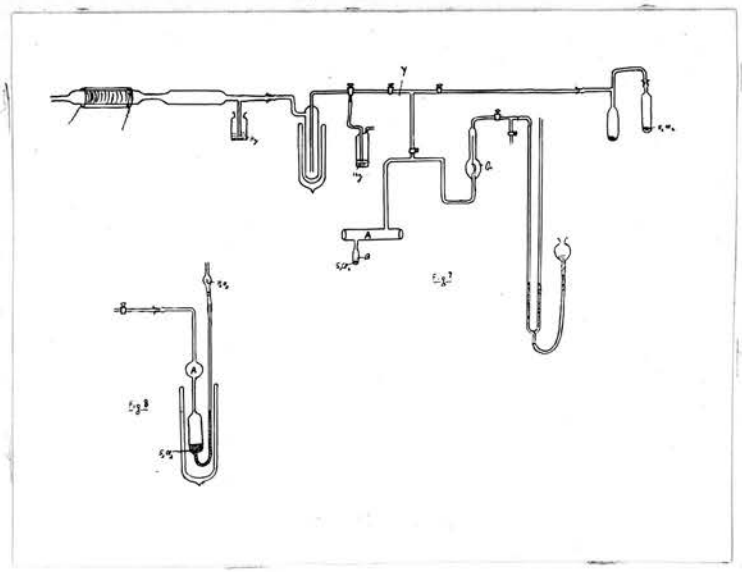
King's Buildings,

Edinburgh University.

April, 1932.

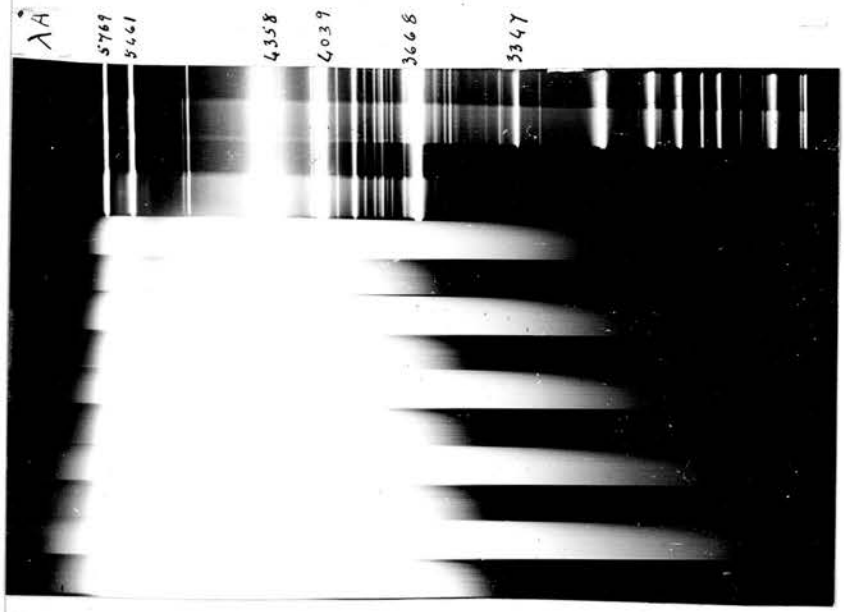
Figures referred to in Part IV





Absorption Spectrum of "S_2Cl_2" Vapour

The Source of Light is a Tungsten Filament Lamp

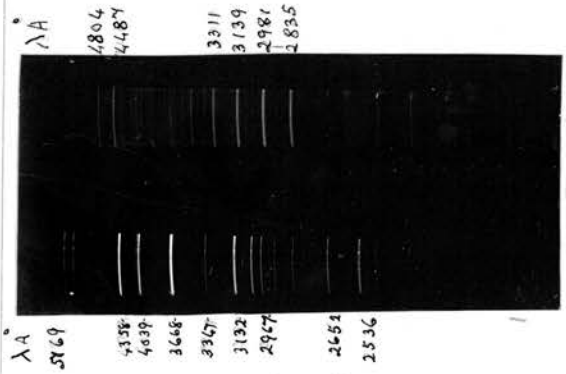


	Exposure
Hg Vapour Lamp	10 sec
Hg Vapour Lamp. Absorption by S_2Cl_2	15 sec / 1 min
Tungsten Lamp Alone	1 min
Absorption by S_2Cl_2	1 min
Lamp Alone	2 min
Absorption by S_2Cl_2	2 min / 3 min
Absorption	3 min / 5 min
etc	5 min / 10 min / 10 min

Plate 1

Emission Spectrum found by passing a discharge through "S_2Cl_2" vapour

(Hilger E.31. Spectrograph)

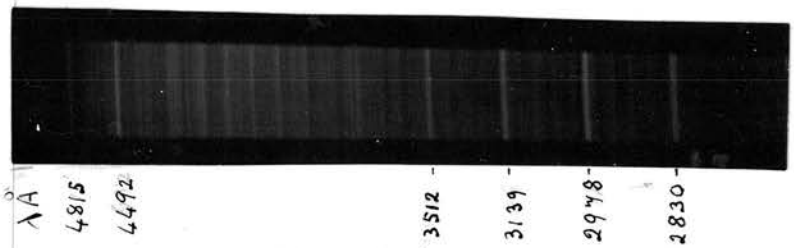


Emission from S_2Cl_2 vapour

Hg Vapour Lamp

Plate 2

Bellingham + Stanley Spectrograph



Emission from "S_2Cl_2" vapour

Plate 3

Air burning in Hydrogen containing a trace of "S_2Cl_2"

Over 6 hours exposure

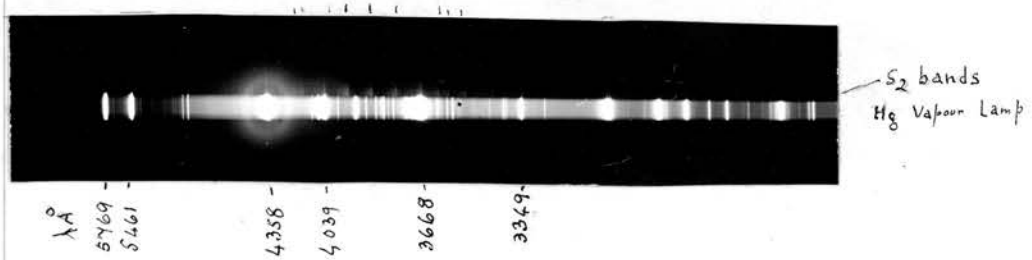


Plate 4

Spectrum of Flames

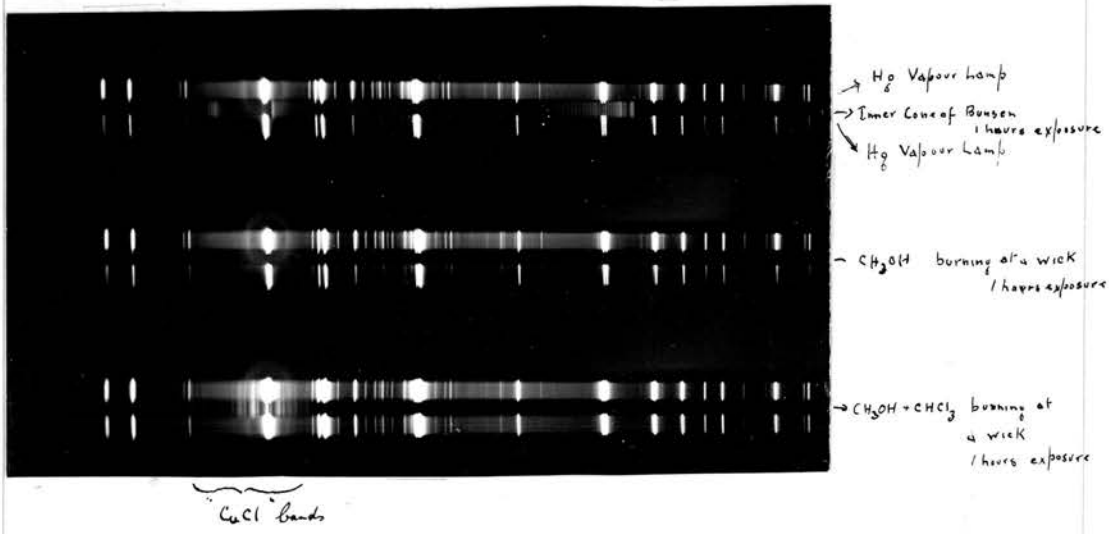


Plate 5

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